

175. (New) A secondary battery according to claim 174, wherein said halide is a fluoride.

176. (New) A secondary battery according to claim 159, wherein said insulating layer comprises at least one element selected from the group consisting of carbon and silicon.

177. (New) A secondary battery according to claim 159, wherein said negative electrode is lithium or a lithium compound and said ion in the battery reaction is a lithium ion.

178. (New) A secondary battery according to claim 159, wherein said negative electrode is zinc or a zinc alloy and said ion in the battery reaction is a hydroxide ion.

REMARKS

This is a division of Application no. 09/163,545, filed to pursue the subject matter of nonelected claims 156-211 from the parent case. Claims 1-122 have been cancelled by the present amendment. Claims 123-155, which were added during the prosecution of the parent application, are not a

part of the present application. Claims 156-211, which were also added while prosecuting the parent application, have been rewritten, as new claims 123-178, with claims 123, 147 and 159 being independent. No new matter has been added.

The title of the invention has been amended to reflect more clearly the subject matter of the present claims.

Accompanying the filing of this Preliminary Amendment and new divisional application are a substitute specification and a marked-up copy of the original specification. The substitute specification is identical to the one previously filed in the parent application, with continuing data added by this amendment. No new matter has been added.

Since the present application is a division of Application no. 09/163,545, their specifications should be identical. This substitute specification will eliminate inconsistencies in the text of any patents that issue from these applications. Moreover, the same substitute specification was filed in a companion Application No. 08/979,464 and its parent Application No. 08/159,141, which is also a parent application of 09/163,545 and a grandparent of the present application.

Consideration of the present claims and passage to
issue are respectfully requested.

Applicants' undersigned attorney may be reached in
our New York office by telephone at (212) 218-2100. All
correspondence should continue to be directed to our below-
listed address.

Respectfully submitted,



Attorney for Applicants

Registration No. 24947

FITZPATRICK, CELLA, HARPER & SCINTO
30 Rockefeller Plaza
New York, New York 10112-3801
Facsimile: (212) 218-2200

NY_MAIN 175924 v 1

marked-up
specification

1

Secondary Battery

BACKGROUND OF THE INVENTION

Field of the Invention

5 The present invention relates to a secondary battery which can repeatedly be used, ~~and more~~ ^{this invention relates} particularly to a reliable secondary battery capable of preventing short circuit ^{growth} ~~occurring~~ due to dendrite ^{even} ~~while~~ ^{if} the battery is repeatedly charged and discharged.

10 Related Background Art

Since global warming is expected ~~to take place~~ ^{by} due to the greenhouse effect caused ~~from~~ ^{by} an increase in CO₂ and so forth, ^{the} construction of thermal power plants ^{has become one of the} encounters problems. Accordingly, it has been considered feasible to perform so-called load levelling for the purpose of effectively using generators by accumulating electric power at night in secondary batteries at homes to level the load.

There ~~arises~~ ^{has arisen} another desire ~~for a~~ ^{to} development of a secondary battery which exhibits a high energy density for use in an electric car that does not exhaust air contamination substances. Further, development of a high performance secondary battery has been needed for use as a power source for portable equipment, such as a book-type personal computer, a word processor, a video camera and a portable telephone.

A locking chair type lithium ion battery capable

1 of serving as the foregoing high performance secondary
battery and comprising a positive pole activating
material comprising lithium ions introduced into an
interlayer compound thereof and a negative pole
5 activating material comprising carbon has been
developed and partially put into practical use.

However the lithium ion battery has not achieved
the high energy density that is the original
characteristics of the lithium battery which uses the
10 metal lithium as the ~~positive~~^{negative} pole activating material.
The reason why a large capacity lithium accumulator of
the type that uses ~~the~~^g lithium metal as the ~~positive~~^{negative}
pole has not been put into practical use is that ~~the~~
generation of dendrites of ~~the~~^g lithium (tree branch-
15 like crystals), which ~~is~~^{are} the main cause of ~~a~~^g short
circuit ~~cannot~~^{ing} be prevented ~~yet~~^g.

The lithium battery, nickel-zinc battery and the
air-zinc battery ~~encounters~~^{are problematic in} that lithium or zinc is, as
described above, deposited on the surface of the
20 negative pole at the time of charge. At this time,
the current density is locally raised on the negative
pole surface depending upon the surface condition,
causing lithium or zinc to be selectively deposited
in the foregoing place. The deposited metal grows
25 (dendrites) in the form of tree branches ~~with the~~^g
~~progress of the charge and discharge cycles~~^{upon charging and discharging}, while
penetrating ~~a~~^{the} separator until it reaches the

1 positive pole, causing a short circuit ~~to occur~~.

The dendrite reaction mechanism is considered as follows. Since lithium or zinc that deposits at the time of charge has a considerable reactivity, it
5 reacts with electrolytic solution or water or the like in the electrolytic solution, causing an insulating film to be formed which has a large resistance. Therefore, the current density in the foregoing portion is raised at the time of the next charge, resulting in ~~that the~~ ^{easy}
10 dendrite ~~can further easily glow~~ ^{growth}. It leads to a ~~fact~~ ^{that} a short circuit ~~takes place~~ ^{between} the negative pole and the positive pole, resulting in that ~~the~~ ^{charging} charge ~~cannot~~ be performed.

If the short circuit ~~has taken place considerably~~ ^{is extensive},
15 the energy of the battery will be consumed in a very short time, causing ~~heat to be generated~~ ^{the generation of}. As a result, the solvent of the electrolytic solution can be decomposed, resulting in ~~generation of gas~~ ^{the}. ~~Therefore,~~
when gas is generated, ~~causing~~ ^{the worst} the internal pressure ~~to be~~ ^{is} raised. In ~~this~~ ^{the worst} case, an accident ~~of an exposure or~~ ^{of} fire can be generated ~~for the worst~~. Therefore, there has been a desire for a long life lithium accumulator that does not easily cause ~~the~~ ^{the} internal short circuit even if the charge and ~~the~~ ^{cycles} discharge are repeated.

25 Also nickel-zinc batteries and air-zinc batteries generate dendrites of zinc due to repetition of charging and discharging, ~~the~~ ^{with} dendrite ~~penetrating~~.

1 the separator. As a result, the zinc negative pole and
the positive pole ^{exhibit} ~~encounter~~ a short circuit. Therefore,
the foregoing conventional technology suffers from an
excessively short cycle life.

5

SUMMARY OF THE INVENTION

An object of the present invention is to provide
a lithium, lithium alloy, zinc or zinc alloy secondary
battery capable of overcoming the foregoing problems
10 ^{associated} ~~experienced~~ with the conventional secondary batteries
and exhibiting a long cycle life.

In order to overcome the foregoing problems ~~of~~
~~experienced with~~ the conventional technology, the
inventors of the present invention have made energetic
15 studies. As a result, ^{it} ~~a fact~~ was found that generation
of dendrites of lithium or zinc can be prevented by
forming a film permitting ions relating to battery
reactions to pass through on the surface of the negative
pole.

20 The present invention is characterized in that a
secondary battery comprises a negative pole made of a
negative pole activating material, a separator, a
positive pole made of a positive pole activating
material, an electrolyte (electrolytic solution), a
25 collecting electrode and a battery case, wherein the
surface of the negative pole is covered with a film
permitting ions relating to battery reactions to pass

1 through.

The material of the film has a molecular structure or small apertures which do not permit the negative pole activating material which precipitates
5 on the negative pole, but which permit ions relating to the battery reactions, to pass through.

The present invention is characterized in that the foregoing material of the film has been electron donative elements or groups for enabling the ions
10 relating to the battery reactions to be easily conducted in the film.

The electron donative element is exemplified by oxygen atoms, nitrogen atoms, sulfur atoms and transition metal atoms, respectively, having a paired
15 electron, a non-paired electron or electron d⁵ (electrons in the d quantum shell). The electron donative group is exemplified by a ring compound and a compound having a carbon double bond
(π electron resonance) having electron π for an aromatic ring.

The film formed on the surface of the negative
20 pole according to the present invention is characterized in that it cannot be dissolved by the electrolyte.

The inventor of the present invention found ~~a~~
~~fact~~ that treatment of the surface of the negative pole with a nitrogen compound or a halogen compound, which is
25 active in a gas phase, will prevent the generation of lithium dendrites.

According to the present invention, there is

1 provided a secondary battery having a negative pole
activating material composed of lithium, a separator,
a positive pole activating material, an electrolyte, a
collector and a battery case, wherein at least the
5 surface of the lithium negative pole opposing the
positive pole is treated with ^a reactive and gaseous
material containing nitrogen or a halogen element.

According to the present invention, there is
provided a battery comprising a negative pole, a
10 separator, a positive pole and an electrolyte, wherein
one or more layers selected from a group consisting of
a conductor layer, a semiconductor layer and an
insulating layer are formed between the negative pole
and the separator.

15 If the negative pole activating material is
lithium or lithium alloy, the foregoing layer is formed
into a micropore structure having small apertures
permitting at least lithium ions to pass through. If
zinc or zinc alloy is used, the small apertures
20 permit hydride ions to pass through.

The small apertures permitting ions to pass
through may be realized by the molecular structure of
the material or by a manufacturing method. The small
apertures can be easily formed by, for example,
25 injecting an electrolyte into the foregoing layer at
the time of forming the layer to manufacture the battery,
the electrolyte being eluting^{ed} to form the micropores.

1 Another method may be employed in which a foaming
material is added at the time of forming the foregoing
layer, ^{with} ~~and then~~ the micropores ^{being} ~~are~~ formed by heat
treatment or the like.

5 The structure of the stacked layers may be a
single layer or a multi-layer composed of two or more
layers or composed of a conductor layer, a semiconductor
layer, an insulating layer and a composite layer
containing two or more types of elements or compounds.

10 Further, ^{it} ~~a fact~~ was found that ^a ~~the~~ separator
partially including a film-shaped member (hereinafter
sometimes called a "metal oxide film") of a metal oxide
formed by a mold made of a bimolecular film forming
compound is able to prevent short circuit ^{from} ~~in~~ the battery
15) ¹ occurring between the negative pole and the positive
pole, ^{where} ~~if~~ dendrites ^{are} ~~is~~ generated in the negative pole.

According to the present invention, there is
provided a secondary battery comprising a negative pole
made of a negative pole activating material, a positive
20 pole made of a positive pole activating material and a
separator which separating ^{es} ~~ing~~ the positive pole activating
material and the negative pole activating material from
each other, wherein at least a multi-layer metal oxide
is present between the positive pole and the negative
25 pole.

^{Also it} ~~Another fact~~ was found that an arrangement ^{wherein the} ~~that~~
surface of the positive pole is covered with a thin film

1 provided a lithium secondary battery at least
comprising a negative pole activating material, a
separator, a positive pole activating material through
which ions can be introduced/discharged due to charge/
5 discharge, an electrolyte which is an ion conductor, a
collecting electrode and a battery case, wherein the
main component of the positive pole activating material
13104 is a compound of one or more types of transition
metal and a group ^{VIA}~~6A~~ element and having a crystal grain
10 size of 500 Å or less.

The main component material of the positive pole
activating material has a structure of an aggregate
selected from a group consisting of amorphous,
microcrystal, a mixture of amorphous, microcrystal and
15 a mixture of amorphous, microcrystal and multi-crystal.

The arrangement ^{wherein} ~~that~~ the positive pole activating
material of the lithium secondary battery is made of a
compound of the transition metal having a structure of
the aggregate selected from a group consisting of
20 amorphous, microcrystal, a mixture of amorphous and a
microcrystal and a mixture of an amorphous, a
microcrystal and a multi-crystal, and the group ^{VIA}~~6A~~
element and having a crystal grain size of 500 Å or
less, more preferably 200 Å, enables the following
25 effects to be obtained:

(1) Since the reactive area of the positive
pole activating material can be enlarged, the

1 electrochemical reactions at the time of charge and
discharge can be made smooth, and therefore the
chargeable capacity can be enlarged.

(2) The introduction and the discharge of
5 lithium ions at the time of the charge and the discharge
prevent the distortion of the positive pole activating
material, causing the cycle life to be lengthened.

It is preferable that the specific area of the
positive pole activating material mainly composed of the
10 compound of the transition metal and the group ~~6A~~⁹ VIA
element be $50 \text{ m}^2/\text{g}$ or more in a state before the
material is formed into the positive pole, more
preferably $100 \text{ m}^2/\text{g}$ or more.

The employment of the compound of the transition
15 metal and the group ~~6A~~^{VIA} element containing hydrogen will
improve ~~in~~⁹ the charge and discharge cycle
characteristics.

By subjecting the positive pole activating
material to a lipophilic treatment using an organic
20 metal compound, the solid-liquid reactions between the
electrolyte and the positive pole activating material
can be made further smooth at the time of charge and
~~the~~⁹ discharge.

The compound of the transition metal and the
25 group ~~6A~~^{VIA} element is exemplified by a metal oxide such
as a nickel oxide, a cobalt oxide, a titanium oxide, an
iron oxide, a vanadium oxide, a manganese oxide,

1 a molybdenum oxide, a chrome oxide or a tungsten oxide,
a metal sulfide such as a molybdenum sulfide, an iron
sulfide or a titanium sulfide, a hydride such as an
oxy iron hydride or their mixtures.

5 By employment of metal lithium having a film
through which lithium ions are able to pass to form
the negative pole activating material of the secondary
battery, a lithium secondary battery exhibiting a long
life and a high energy density can be obtained.

10 According to the present invention, there is
provided a method of manufacturing a positive pole
activating material of a lithium secondary battery at
least comprising the step of forming a compound of a
transition metal and a group ~~6A~~^{VIA} element, the raw
15 material of which is one or more types of materials
selected from a group consisting of the transition
metal, the salt of the transition metal, an organic
metal compound of the transition metal, a hydride of the
transition metal, a ~~hydrogated~~ transition metal, ^{oxide} a
20 carbonyl compound of a transition metal and a transition
metal oxide and which has a structure of an aggregate
having a crystal grain size of 500 Å or less, more
preferably 200 Å or less and selected from a group
consisting of amorphous, microcrystal, a mixture of
25 amorphous and microcrystal and a mixture of amorphous,
microcrystal and multi-crystal.

According to the present invention, there is

1 provided a method of manufacturing a positive pole
activating material which is a compound of a transition
metal and a group ^{VIA}~~6A~~ element, the method comprising the
steps of:

5 employing one or more types of reactions
selected from a group consisting of a reaction between
a salt of the transition metal and alkali, a hydrolysis
decomposition reaction of an organic transition metal
compound and a reaction between the transition metal and
10 alkali to prepare a hydride of the transition metal;

employing a dehydrating reaction or decomposition
of the salt of the transition metal or the organic
transition metal compound in a gas phase or a reaction
between the salt of the transition metal or the
15 decomposed material of the organic transition metal
compound or vapor of the transition metal and the group
^{VIA}~~6A~~ element or the group ^{VIA}~~6A~~ compound;

melting one or more types of materials selected
from a group consisting of the transition metal and the
20 transition metal compound to be allowed to react with
one or more types of materials selected from a group
consisting of the group ^{VIA}~~6A~~ element and the compound of
the group ^{VIA}~~6A~~ element; and

rapidly cooling the materials to form an
25 aggregate having a crystal grain size of 500 Å or less
and formed into a structure selected from a group
consisting of amorphous, microcrystal, a mixture of

- 1 amorphous and microcrystal and a mixture of amorphous,
microcrystal and multi-crystal.

BRIEF DESCRIPTION OF THE DRAWINGS

- 5 Fig. 1 is a basic structural view which
illustrates a secondary battery according to the
present invention;

- Fig. 2 is a schematic cross sectional view
which illustrates a flat battery to which the present
10 invention is applied;

- Fig. 3 is a schematic cross sectional view
which illustrates an example of a cylindrical battery
to which the present invention is applied;

- Fig. 4 is a schematic view which illustrates an
15 example of a partial structure of a negative pole
covered with a film through which ions relating to
battery reactions are able to pass;

- Fig. 5 is a basic structural view which
illustrates another embodiment of the secondary battery
20 according to the present invention;

- Fig. 6 is a schematic structural view which
illustrates an apparatus for subjecting lithium for use
in the secondary battery according to the present
invention to surface treatment;

- 25 Fig. 7 is a schematic structural view which
illustrates an apparatus for subjecting lithium for use
in the secondary battery according to the present

At page 14, before line 24, insert

-- As employed herein, the terms "positive pole" or "negative pole" are identical to "positive electrode" or "negative electrode", respectively; the phrase "activating material" is used interchangeably with "active material" and the phrases "electrolytic solution" or "electrolytic liquid" are used interchangeably with "electrolyte solution" or "electrolyte liquid", respectively. --

000000-000000

1 invention to surface treatment;

Fig. 8 is a schematic view which illustrates an effect of the present invention;

5 Figs. 9A to 9H are views which illustrate examples of layer stacking patterns according to the present invention including a conductor layer, a semiconductor layer and an insulating layer between the negative pole and the separator thereof;

10 Fig. 10 is another basic structural view which illustrates the secondary battery according to the present invention;

Fig. 11 is a schematic cross/sectional view which illustrates another cylindrical battery to which the present invention is applied; -/

15 Fig. 12 is another basic structural view which illustrates the secondary battery according to the present invention; and

20 Fig. 13 is another basic structural view which illustrates the secondary battery according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Structure of Battery

(Insert) 1
25 A secondary battery according to the present invention comprises a negative pole, a separator, a positive pole, an electrolyte and a collector. Fig. 1 is a basic structural view which illustrates the

1 secondary battery. Referring to Fig. 1, reference
numeral 100 represents a negative collector, 101
represents a negative pole substantially made of
negative pole activating material, 102 represents a
5 ~~shell~~^{film}, 103 represents a positive collector, 104
represents a positive pole substantially made of
positive pole activating material, 105 represents an
electrolytic solution (electrolyte), 106 represents a
negative terminal, 107 represents a positive terminal,
10 109 represents a case for the secondary battery, and 108
represents a separator. Figs. 5, 10 and 12 illustrate
another basic structure in which a multi-layer oxide
film 10102, an ion permeable film ¹²¹⁰²~~10102~~ and a layer 5102
applied with lithium surface treatment in place of the
15 film 102. If the lithium battery comprises the negative
pole 101 made of the negative active material which
is lithium or lithium alloy, lithium ions in the
electrolytic solution 105 are introduced into the space
between the layers of the positive pole activating
20 material of the positive pole 104 through the permeable
film due to the discharge reaction in a case of the
structure shown in Fig. 12. Simultaneously, lithium
ions are dissolved and discharged from the negative pole
activating material 101 into the electrolyte 105 through
25 the film 102 and the multi-layer metal oxide 10102. In
the charging reaction, lithium ions in the electrolytic^{eq}
solution 105 are, in the form of lithium metal,

1 precipitated into the negative pole activating material
through the film 102 (dendrites can easily ^{grow} grow if the
film 102 is not present). Simultaneously, lithium
between the layers of the positive pole activating
5 material 104 is dissolved and discharged into the
electrolytic solution 105. Although lithium ions
precipitated during the charging reaction are in a very
active state to react with ^a small quantity ^{of} water, oxygen,
impurities or solvent ^{contained} in the electrolyte ^{contained}, the
10 structure in which the surface of the negative pole 101
is covered with the film 102 prevents direct contact
between the precipitated lithium and the electrolytic
solution. Therefore, the generation of dendrites, which
causes ^{the} battery short circuit to occur, can be
15 prevented.

In ^{the} a case of an alkali battery comprising the
negative pole activating material 101 made of zinc or
zinc alloy, the discharge reaction takes place in such a
manner that hydroxyl ions in the electrolytic solution
20 105, similarly to the above, react with the negative
pole activating material 101 of the negative pole 101
through the film 102. Simultaneously, hydroxyl ions are
discharged into the electrolytic solution 105 from the
positive pole activating material of the positive pole
25 104. The charging reaction is performed in such a
manner that hydroxyl ions are discharged from the
negative pole 101 into the electrolytic solution 105

1 through the film 102 (if the film 102 is not present at
this time, zinc ions in the electrolytic solution 105
easily cause dendrites to ^{grow} ~~grow~~ on the negative pole).
Simultaneously, hydroxyl ions in the electrolytic
5 solution 105 react with the positive pole 104.
Similarly to the case where the negative pole activating
material is lithium, the ^{presence} ~~present~~ of the film 102
prevents generation of zinc dendrites at the time of
charging.

10 Therefore, the present invention is able to
prevent short circuits in the battery, lengthen the life
of the secondary battery and improve ~~the~~ safety.

If the foregoing negative pole activating
material is lithium or lithium alloy, lithium ions are
15 used in the reactions in the battery. In the case of
the alkali battery containing zinc as the negative pole
activating material, hydroxyl ions are used in the
reactions. The batteries comprising zinc as the
negative pole activating material is typified by nickel-
20 zinc battery, air-zinc battery and bromine-zinc battery
(however, the bromine-zinc battery comprises zinc ion
as the negative side ion that ^{is} ~~are~~ used in the inside
reactions).

Method of Forming Negative Pole

25 The negative pole can be formed by any one of
the following methods as well as the method for
forming the same by directly covering the surface of

1 the negative pole activating material with a coating material by a dipping method, a spraying method or a CVD method.

5 It is effective to employ a method in which a conductive and porous matrix (the base), for example, a sponge-like or ^{fibrary} ~~fiber~~ metal or carbon~~o~~ having communication holes, is covered with a coating material through which ions for use in the reactions in the battery can be passed through, and then lithium or zinc, 10 which is the negative pole activating material, is caused to ^{electro-deposit} ~~electrochemical precipitate and adhere~~ so that the negative pole is formed. If a porous and conductive matrix has a wide specific area, the current density per unit area at the time of ~~the~~ charge and ~~the~~ 15 discharge can be lowered. Therefore, the growth of ~~the~~ dendrites can be prevented and accordingly the charging/ discharging efficiency^{cy} can be improved.

It is preferable that the film made of a coating material, through which ions can be passed through, ^{wherein} ~~the~~ 20 small apertures serving^e as the spaces, in which the lithium can be ^{deposited} ~~precipitated~~, be formed into a 3D net shape.

Another effective method may be employed which ^{includes} ~~has~~ steps of directly immersing a porous and conductive 25 matrix in the melted negative pole activating material, taking out the matrix, covering the surface of the conductive matrix with the negative active material or

1 electrochemically covering the same with the negative
pole activating material, and applying a coating
material through which ions for use in the reactions in
the battery can be passed to the surface.

5 Fig. 4 is a schematic view which illustrates a
partial structure of a negative pole formed by covering
a conductive matrix 400 with a negative pole activating
material 401 and a coating material 402 through which
ions for use in the reactions in the battery can be
10 passed.

Material for Covering the Surface of Negative Pole

The coating material for covering the surface of
the negative pole will now be described (1 to 7).

1. Film Having an Inorganic Glass Structure

15 By covering the surface of the negative pole
activating material with ^athe film having an inorganic
glass structure, through which ions for use in the
reactions in the battery can be passed, the reactions
between lithium and water or oxygen can be prevented,
causing ^{ease}~~ease~~ in handling if the negative pole
20 activating material is lithium. Further, the direct
contact between the lithium and the electrolytic
solution does not take place. Therefore, the growth of
the polymer film formed from the solvent of the
25 electrolytic solution on the surface of lithium can be
prevented. If the negative active material is zinc, the
elution of zinc into the electrolytic solution can be

1 prevented. As a result, formation of dendrites can be
prevented and therefore the cycle life against charge
and discharge can be lengthened. Since the film having
the inorganic glass structure is flame retardant or
5 incombustible, safety in an emergency breakage or the
like can be improved. The foregoing inorganic glass may
be made ^{of} any ~~one of a~~ ^{oxide} metal oxide selected from ~~a~~ ^{the} group
consisting of silica, titanium oxide, alumina, zirconia
oxide, magnesium oxide, tantalum oxide, molybdenum
10 oxide, tungsten ~~molybdenum~~ ^{oxide}, tin oxide, indium oxide,
iron oxide, chrome oxide, aluminum phosphate, iron
phosphate, silicon phosphate and their mixtures. In
particular, it is preferable to employ silica, titanium
oxide, alumina, zirconia oxide or aluminum phosphate.

15 A sol-gel method is one ~~of~~ ^{of} adequate methods for
forming the inorganic glass. However, ~~the fact that~~ ^{the}
~~due to lithium has a low melting point of (181°C) causes a~~ ^{of lithium,}
~~necessity to arise for the operation of directly~~
~~applying the foregoing material to the surface of~~ ^{must be directly applied}

20 lithium ~~to be performed~~ ^{such that} at low temperature. Since
lithium reacts with water and alcohol, the operation
must be performed ~~in a circumstance in which~~ ^{in which} no water
and alcohol is present (the case in which the inorganic
glass is previously applied to the conductive matrix or
25 the case where the negative pole activating material is
zinc are excluded).

Therefore, the sol-gel method, which is the typical

1 inorganic coating method at low temperature, must be
performed with any particular means. The raw material
for the material having the inorganic glass structure is
obtained in such a manner that an acid or a base and
5 water are added to a solution of alcohol of an organic
metal compound such as a metal alkoxide to hydrolyze the
raw material so as to form colloid particles having
metal atom-oxygen atom bonds, and then the solvent is
substituted by a non-hydric solvent except alcohol.

10 The surface coating of the negative pole activating
material is formed in a manner comprising steps of
directly applying the foregoing colloid solution, or
applying a solution, in which a monomer or an organic
polymer or both organic polymer and a crosslinking
15 material are dissolved in the colloid solution, and
polymerizing it or drying and hardening it. By
combining the organic polymers, strength against cracks
and separations can be improved. If the electrolyte for
forming the battery is dissolved in the colloid solution
20 to form the film, wettability with the electrolytic
solution can be improved, causing ions to be moved
easily.

As an alternative to alkoxide, any one of the
following organic metal compounds may be employed:

25 acetyl acetone salt, an alkyl metal compound, acetyl
acetone metal salt, ^{naphthene} ~~naphthene~~ acid metal salt, and
octyl acid metal salt.

The polymer crosslinking material is exemplified by diisocyanate, polyisocyanate prepolymer, block isocyanate, organic peroxide, polyamine, oxime^e, nitroso compound, sulfur or sulfur compound, selenium, magnesium oxide, lead oxide and zinc oxide. As an alternative to using the crosslinking material, a method may be employed in which radial rays or electron rays or ultraviolet rays are applied to polymerize or crosslink the polymer.

15 As an application method, a dipping method, screen printing, spraying or a roll coating method may be employed. The viscosity of the liquid to be applied must adequately be adjusted to be adaptable to the application method.

20 In order to facilitate the movement of the charge at the time of the charging operation, powder or fiber or whisker of conductive material such as carbon or titanium may be mixed with the foregoing film forming solution.

25 It is preferable that the thickness of the film to be formed on the surface of the negative pole activating material ranges from 50 Å to 100 μ, further preferably

1 ranges from 100 Å to 10 μ. The optimum thickness of the film differs depending upon the density or the ~~void~~ porosity ratio of the film and considerably differs depending upon the type of the electrolytic solution.

5 The thickness of the film can be adjusted by changing the concentration of the main material in the coating liquid for forming the film.

2. Polymer Film of Derivative of Aromatic Hydrocarbon Compound

10 By covering the surface of the negative pole activating material with a polymer film of a derivative of an aromatic hydrocarbon compound, the reaction between lithium and water or oxygen can be prevented in the case where the negative pole activating material is
15 lithium. ~~It leads to a fact that~~ ^{in this way} handling can be facilitated. Further, the contact between lithium and electrolytic solution can be prevented. Therefore, the growth of a polymer film, which is formed from the solvent of the electrolytic solution, on the surface of
20 lithium can be prevented. If the negative pole activating material is zinc, elution of zinc into the electrolytic solution is prevented by the film.

As a result, formation of dendrites can be prevented and therefore the life against the charge and discharge
25 cycle can be lengthened. The derivative of the aromatic hydrocarbon for forming the charge moving complex with lithium is one or more derivatives selected from ~~a~~ ^{the} group

1 consisting of naphthalene, anthracene, ~~phenanthrene~~^{phenanthrene},
naphthalene, pyrene, triphenylene, ~~perylene~~^{perylene}, picene,
benzopyrene, coronene and ovalene. The polymer for use
to form the coating material can be prepared by
5 polymerization or copolymerization of vinyl monomer,
monomer of acetylene derivative or dicarboxylic acid and
a monomer such as glycol. The polymerization of the
vinyl monomer can be performed by radical or ion
polymerization. The monomer of the acetylene derivative
10 can be polymerized while using a chloride of tungsten as
a catalyzer. The dicarboxylic acid and diamine can be
polycondensed, and the dicarboxylic acid and glycol can
~~as well as~~^{as well} be polycondensed. The monomer of the
aromatic derivative for forming the polymer is
15 exemplified by 2 - vinyl naphthalene, 2 - vinyl
pyridine, 9 - vinyl anthracene, 9, 10 - anthracene
dipropionic acid, 9, 10 - bis (phenyl ethyl) anthracene
and 5, 12 - bis (phenyl ethynyl) naphthalene. It is
preferable to use 2 - vinyl naphthalene or 9 - vinyl
20 anthracene.

A starting material for the radical polymerization
is exemplified by azobisisobutyronitrile^{if} (AIBN),
benzoylperoxide (BPO) and t-butylhydroperoxide. A
starting material for the cation polymerization is
25 exemplified by an acid such as H_2SO_4 , H_3PO_4 , $HClO_4$,
 CCl_3 or CO_2H and ^aFriedel-Craft catalyst^x such as BF_3 ,
 $AlCl_3$, $TiCl_4$ or $SnCl_4$. A large ring compound having

- 1 an aromatic ring can be polymerized by dehydrogenation
in which the Friedel-Craft catalyzer and an oxidizer are
combined ^{with} ~~to~~ each other. A starting material for the
anion polymerization may be an alkaline metal compound
5 or an organic metal compound.

As an alternative to the foregoing method, a
polymer into which an aromatic group ^{can be substituted} ~~can~~ be obtained by
subjecting the side chain of each polymer to a
substitution reaction with a derivative of an aromatic
10 compound. Another method may be employed in which an
electrolytic polymerization reaction is ^{performed} ~~caused to take~~ ~~place~~
in an electrolytic solution containing a monomer
mixed therein to form directly a polymer of an aromatic
compound on the surface of lithium.

- 15 When the surface of lithium is ~~applied with a~~
^{coated} ~~coating by~~ using the foregoing polymer solution, it is
preferable to use a polymer solution dehydrated and
deoxidized sufficiently in inactive gas ~~dehydrated~~
^{sufficiently}. It is preferable to use a solvent in the
20 foregoing solution which has been dehydrated with active
alumina, molecular ^{sieve} ~~sheave~~, phosphorus pentaoxide or
calcium chloride. As an alternative to this, it is
preferable, depending upon the type of ~~the~~ solvent, that
the solvent be distilled ^{in the} ~~under~~ presence of alkaline
25 metal in inactive gas to remove impurities and ~~to~~ be
dehydrated (however, the necessity of strictly
controlling water can be eliminated when the polymer is

1 previously applied to the conductive matrix or when the
negative pole activating material is zinc).

An electrolyte may previously be mixed when the
foregoing film is formed. ~~It leads to a fact that~~
5 Wettability between the electrolytic solution and the
film can be improved^{in this way}, causing ions to easily pass
through the film. In order to facilitate the ~~movement~~^{transfer}
of the charge at the time of charging, conductive
powder, such as carbon or titanium, fiber or whisker may
10 be mixed at the time of forming the film.

Since the performance of the battery deteriorates
if the polymer coating film is dissolved in an organic
solvent of the electrolyte, it is preferable to be
crosslinked in such a manner, for example, ultraviolet
15 rays, electron rays or radial rays are applied or a
crosslinking material, such as a radical generating
agent, is used.

It is preferable that the thickness of the film to
be formed on the surface of the negative pole activating
20 material ranges from 50 Å to 100 μ^{and} more preferably
ranges from 100 Å to 10 μ.

The optimum thickness of the film differs depending
upon the density or the ~~void ratio~~^{porosity} of the film and
considerably differs depending upon the type of the
25 electrolytic solution. The thickness of the film can be
adjusted by changing the concentration of the main
material in the coating liquid for forming the film.

1 3. Organic Metal Compound

When the surface of lithium and ^{an} ~~the~~ organic metal compound react with each other, bonding with lithium atoms takes place so that a film having a surface which
5 is organic-bonded is formed. As a result, the wettability (the lipophilic property) is improved, causing lithium ions to be easily introduced/discharged at the time of the charge and discharge. Further, the surface coating film prevents ~~the~~ ^{and therefore} direct contact between
10 lithium and the organic solvent, ~~causing~~ the formation ^e ~~on the surface of lithium~~ of a polymerized film of the organic solvent, which increases the resistance ^{so} ~~in~~ the battery, can be prevented. As a result, formation of dendrites ^g can be prevented, and therefore life against
15 the charge and discharge cycle can be lengthened. Further, reactions between lithium and water during the manufacturing process can be prevented and accordingly handling can be made easier. If the content of lithium in the film is high in the lithium battery according to
20 the present invention, rapid reactions of lithium at an emergency breakage can be prevented.

The foregoing organic metal compound may be a material selected from ^{the} ~~a~~ group consisting of: metal alkoxide, alkaline metal compound, acetyl acetone metal
25 salt, naphthene acid metal salt, or ^{octyl} ~~octyl~~ acid metal salt of metal, such as titanium, aluminum, silicon, zirconium, tantalum, magnesium, indium, tin, molybdenum,

- 1 tungsten or germanium. Among the foregoing organic
metal compounds, it is preferable to use a metal
compound of silicon or titanium or aluminum ~~because of~~ *due to*
ease of film formation ~~easy forming of the film~~ and excellent stability of the
5 formed film.

- The organic silicon compound may be alkoxysilane,
alkylsilane, halogenated silane, siloxane, silane
containing vinyl group, amino group, epoxy group,
methacrylic group or mercaptal group introduced thereto,
10 hydrogen - denatured, vinyl - denatured, hydroxyl group
denatured, amino - denatured, carboxylic group
denatured, chloro - denatured, epoxy denatured,
methacryloxy ~~methachryloxy~~ - denatured, mercapto - denatured,
fluorine - denatured, long - chain - alkyl denatured
15 or phenyl - denatured polysiloxane, alkylene oxide
denatured siloxane copolymer, silicon - denatured
copolymer, alkoxysilane - denatured polymer, silicon -
denatured urethane or silicon - denatured nylon.

- The organic titanium compound may be
20 alkoxytitanium, titanium chelate, titanium *acrylate* ~~acylate~~ or
titanium polymer.

The organic aluminum compound may be
alkoxyaluminum, alkylaluminum or a halogenated aluminum.

- The organic silicon-titanium compound may be a
25 tyranopolymer of a silicon polymer crosslinked to the
main chain of a polycarbosilane skeleton with a titanium
compound.

1 Also a material prepared by introducing a
derivative of an organic metal compound into a polymer
by substitution may be used as the coating material.

5 The film may be formed by directly applying the
organic compound or by applying it after ^{diluting} ~~diluted~~ with a
solvent if the organic compound is in the form of
liquid. If the organic compound is in the form of a
solid, a solution ^{an appropriate} ~~dissolved~~ in a solvent can be applied.
The organic compound may be applied by dipping, screen
10 printing, spraying or roll coating. The viscosity of
the foregoing coating liquid must adequately be adjusted
to be suitable for the employed coating method.

15 By mixing the organic metal compound at the time
of forming the film, the wettability of the electrolytic
solution can be improved and accordingly ions can easily
be introduced/discharged at the time of the charge and
~~the~~ discharge. Further, the ^{transfer} ~~movement~~ of the charge can
be made easier at the time of the battery charge by
mixing powder or fiber or whisker of conductive material
20 such as carbon or titanium at the time of applying the
organic metal compound.

25 It is preferable that the thickness of the film
to be formed on lithium ranges from 50 Å to 100 μ ^{and} more
preferably ^{from} 100 Å to 10 μ. The optimum thickness of the
film differs depending upon the density or the ~~void~~ ^{porosity}
~~ratio~~ of the film and considerably differs depending
upon the type of the electrolytic solution. The

1 thickness of the film can be adjusted by changing the
concentration of the main material in the coating
liquid for forming the film.

4. Fluororesin Coating Material

5 By using fluorine resin of a type having an ether
bond to cover the surface of lithium, the surface
coating process can be completed easily and the contact
between lithium and the film can be improved.

The presence of oxygen atoms ⁱⁿ of the fluorine
10 resin having the ether bond makes easier the coordination
of lithium ions, enabling lithium ions to be moved
easily in the fluorine resin.

Further, the surface coating film prevents the^e
direct contact between the lithium metal and the organic
15 solvent, and therefore the formation of a polymerized
film of the organic solvent, which increases the
internal resistance of the battery, on the surface of
lithium can be prevented.

As a result, the formation of dendrite^s can be
20 prevented and therefore the life against the charge and
discharge cycle can be lengthened.

By covering the surface of lithium with the
fluorine resin, reactions of lithium with water or
oxygen can be prevented, ^{facilitating} ~~causing~~ handling to be^e
25 ~~facilitated.~~

Since the fluorine resin is a flame retardant
resin, it ^{promotes} ~~exhibits~~ safety ^{with respect to} ~~at the time of~~ an emergency

1 fire accident.

The fluorine resin for covering the surface of lithium is exemplified by: a copolymer with a vinyl monomer, such as vinyl ether, dioxysol, dioxyne or
5 dioxyene having an ether bond with fluoroethylene or diene monomer derivative or a copolymer with a vinyl monomer, such as vinyl ether, dioxysol or dioxyne, ⁰dioxyene having a fluorized ether bond with a diene compound, such as ethylene. In particular, it is
10 preferable to use a copolymer with vinyl ether having an ether bond with fluoroethylene. The fluoroethylene may be a fluoroethylene derivative such as tetrafluoroethylene, chlorotrifluoroethylene, vinylidene fluoride or vinyl fluoride. The fluoroethylene
15 copolymer containing the ether bond can be polymerized by a solution, suspension, block or emulsion polymerization. As a starting material, a peroxide, alkyl boron, light or radial rays may be employed.

The fluororesin can be coated on lithium metal
20 by any one of the following methods:

a. A solution of the fluororesin is applied by spraying, screen printing, by using a coater or by dipping.

b. The fluororesin is directly coated to the
25 surface of lithium by a vacuum evaporation method such as sputtering.

c. A polymer film is directly formed by plasma

- 1 polymerization under an atmosphere of monomer which is
the raw material for the fluororesin.

- If the lithium surface is coated by using the
fluororesin solution, it is preferable to use, in an
5 inactive gas dehydrated sufficiently, a fluororesin
solution dehydrated and deoxidized sufficiently. It is
preferable to use a solvent in the foregoing solution
which has been dehydrated with active alumina, molecular
~~sheave~~^{sieve}, phosphorus pentaoxide or calcium chloride. As
10 an alternative to this, it is preferable depending upon
the type of the solvent that the solvent be distilled
under presence of alkaline metal in inactive gas to
remove impurities and to be dehydrated. However, the
necessity of strictly controlling water can be
15 eliminated when lithium is electrochemically inserted
and allowed to ~~adhere~~^{deposit} between the fluororesin and the
conductive matrix.

- An electrolyte may previously be mixed when the
foregoing film is formed. ~~It leads to a fact that~~
20 Wettability between the electrolytic solution and the
film can be improved^{in this way}, causing ions to ~~easily pass~~
through the film. In order to facilitate the ~~movement~~^{transfer}
of ~~the~~^{the} charge at the time of charging, conductive
powder, such as carbon or titanium, fiber or whisker
25 may be mixed at the time of forming the film.

Since the performance of the battery
deteriorates if the fluororesin film is dissolved in

1 an organic solvent of the electrolytic solution, it is
preferable that the film is crosslinked.

As an alternative to the foregoing method of
coating the lithium surface with the fluororesin
5 solution, another method may be employed in which a
fluorocompound, such as tetrafluoroethylene is
polymerized with the main raw material with plasma to
be applied to the surface. It is preferable to employ
another method for improving the contact and strength
10 of the film in which oxygen, hydrogen, helium, argon,
nitrogen, silane, hydrocarbon or the like is mixed with
the fluorocompound which is the main material. The
plasma can effectively be generated by a DC or RF glow
discharge method, a microwave discharge method or a
15 laser beam irradiation method.

It is preferable that the thickness of the film
to be formed on the surface of lithium ranges from 50 Å
to 100 μ^m and more preferably ranges from 100 Å to 10 μ.
The optimum thickness of the film differs depending upon
20 the density or the ^{porosity} ~~void ratio~~ of the film and
considerably differs depending upon the type of the
electrolytic solution. The thickness of the film can
be adjusted by changing the concentration of the main
material in the coating liquid for forming the film.

25 5. Large Ring Compound

By coating the surface of the negative pole
activating material with a large ring compound through

1 which ions for use in the reactions in the battery can
be passed, the reactions between lithium and water or
oxygen can be prevented if the negative active material
is lithium. As a result, handling can easily be
5 performed. Further, the direct contact between lithium
and the electrolytic solution can be prevented, and
therefore the growth of a polymer film on the surface of
lithium to be formed from the solvent of the electrolytic
solution can be prevented. If the negative pole
10 activating material is zinc, the dissolution of zinc
into the electrolytic solution can be prevented. As a
result, the formation of dendrites can be prevented,
causing the life against the charge and discharge cycle
to ~~can~~ be lengthened.

15 The large ring compound is a large ring compound
having heteroatoms composed of one or more types of
atoms selected from a group consisting of oxygen,
nitrogen and sulfur. In order to ^{pass} ~~cause~~ ions for use
in the reactions in the battery ~~to be passed~~
20 satisfactorily, a compound having one or more structures
selected from a group consisting of ring polyether, ring
polyamide, ring polythioether, azacrown ether, ring
thioether, thiocrown ether, cryptand, cycrum, nonactyne
and bariomicine each having a hole having a ^{radius larger} ~~radius larger~~
25 than the ^{radius} ~~radius~~ of ions to be used in the reactions in
the battery, thyracrown, cyclodextrin, cyclophane,
~~phthalocyanine~~ ^{phthalocyanine} and porphyrin each of which is ^a ~~a~~ crown

- 1 ether having silicon atoms. It is preferable to use crown ether polymer, bariomicine, phthalocyanine or ~~porphyrin~~ ^{porphyrine} porphyrin.

- By covering the surface of the negative pole
- 5 activating material with the large ring compound, the ~~movement~~ ^{transfer} of ions for use in the battery reactions between the electrolytic solution and the negative pole activating material can be made easier. Therefore, local generation of zinc or lithium dendrites on the
- 10 negative pole can be prevented. Further, reactions between fresh lithium or zinc generated at the time of the charge with the solvent of the electrolytic solution can be prevented.

- The surface coating of the large ring compound
- 15 to be applied to the surface of the negative active agent can be performed in any of the following methods:

- a. A polymer solution obtained, by polymerization, from the derivative of the large ring compound is applied by dipping, spraying, screen printing ^{or} ~~and~~ coater
- 20 coating.

b. A mixture of the binder polymer and the derivative of the large ring compound is applied, and then it is crosslinked so that the film is formed.

- c. The derivative of the large ring compound
- 25 is, as a monomer, dissolved in an electrolytic solution, an electric field is applied to the solution, and then the film is formed on the surface of the negative pole

1 activating material or the conductive matrix by
electrolytic polymerization.

d. Lithium is immersed in a solution of the
derivative of the large ring compound, which can be
5 anion-polymerized by lithium, so that the polymer film
is formed.

e. A polymer is applied, the polymer being
obtained by heating and condensing a large ring
compound having an aromatic ring and formaldehyde in
10 ~~a~~ formic acid.

f. The film is formed by sputtering the large
ring compound or the polymer of the same or by plasma-
polymerizing the same.

An electrolyte may be mixed at the time of
15 forming the foregoing film. As a result, the
wettability between the electrolytic solution and the
film can be improved, causing ions to be easily passed
through the film. In order to facilitate the ~~movement~~^{transfer}
of ~~the~~ charge at the time of the charging operation,
20 powder or fiber or whisker of conductive material such
as carbon or titanium may be mixed at the time of
forming the film.

As the polymer for use in the coating solution,
poly [(dibenzo - 18 - crown - 6) - coformaldehyde] or
25 the like can be used. A polymer for coating can ~~newly~~^{newly}
be prepared by the following polymerization reactions.
By condensation polymerization of a large ring compound

1 having, at the terminative group thereof, carboxylic
group or amino group or a hydroxyl group, polyamide can
be obtained if the carboxylic group and the amino group
react with each other. Polyester can be obtained if
5 the carboxylic group and the hydroxyl group react with
each other. The vinyl compound of the large ring
compound or diene of the large ring compound enables an
additive polymer to be obtained by radical polymerization,
cation polymerization or anion polymerization. The
10 starting material of the radical polymerization may be
azobisisobutyronitrile (AIBN), benzoylperoxide (BPO) or t-
butylhydroperoxide. A starting material for the cation
polymerization is exemplified by an acid such as H_2SO_4 ,
 H_3PO_4 , $HClO_4$, CCl_3 or CO_2H and Friedel-Craft catalyst
15 such as BF_3 , $AlCl_3$, $TiCl_4$ or $SnCl_4$. A large ring
compound having an aromatic ring can be polymerized by
dehydrogenation in which the Friedel-Craft catalyst and
an oxidizer are combined with each other. A starting
material for the anion polymerization may be an alkaline
20 metal compound or an organic metal compound.

As the monomer of the large ring compound for use
in the polymerization may be crown ether/(+) - 18 -

crown - 6 - tetracarboxylic acid, 1, 5, 9, 13, 17, 21 -
hexathia cyclotetrasiloxane - 3, 11, 19 - triol, 1, 5, 9,
25 13 - tetrathia cyclohexadecan - 3, 11 - diol, 1 - aza -
12 - crown - 4, 1 - aza - 15 - crown - 5, 1 - aza - 18 -
crown - 6, 1, 4, 10, 13 - tetraoxo - 7, 16 -
tetraoxo

~~diazocyclooctadecane~~
1 ~~diazocyclooctadecan~~, 1, 4, 10 - trioxa - 7, 13 -
~~diazocyclopentadecane~~
~~diazocyclopentadecan~~, or 6, 8 - dioxabicyclo [3. 2. 1] -
~~oxetane~~
~~oxane~~ - 7 - on. As an alternative to this,
dibenzocrown ether can be used.

5 In the foregoing polymerization, a copolymer of
two more types of derivatives of the large ring compounds
or a copolymer of the large ring compound and another
monomer may be used as well as the polymer of the
derivatives of the large ring compounds. A polymer
10 obtainable by introducing the derivative of the large
ring compound into a polymer by substitution may be
employed.

When a battery is manufactured, a polymer must be
selected so as not to be dissolved in the solvent of the
15 electrolytic solution or the polymer crosslinking
reactions are caused to proceed so as not^{to} be dissolved
in the electrolytic solution.

The derivative of the large ring compound having,
^{as e} at the terminative group thereof, carboxylic group or
20 amino group or a hydroxyl group or having a vinyl bond
or a diene bond and a crosslinking material are mixed in
the polymer serving as the binder, and then the mixed
material is hardened. The crosslinking material is
selected from ^{the} a group consisting of diisocyanate, a
25 polyisocyanate prepolymer, block isocyanate, an organic
peroxide, polyamine, ^{oximes} oxims, a nitroso compound, sulfur,
a sulfur compound, selen^{ium} a magnesium oxide, a lead

oxide and a zinc oxide. The organic peroxide is exemplified by dicumyl - peroxide, 2, 5 - dimethyl - 2, 5 - di - (t - butyl ~~peroxy~~) hexane, 1, 3 - bis - (t - butyl ~~peroxy~~ isopropyl) benzene, 1, 1 - bis - (t-butyl ~~peroxy~~) - 3, 3, 5 - trimethyl ~~cyclohexane~~, n-butyl - 4, 4 - bis - (t-butylperoxy) valerate, 2, 2 - bis - (t-butyl ~~peroxide~~) butane, t-butyl ~~peroxy~~ benzene, and vinyl - tris - (t-butyl ~~peroxy~~) silane. As an accelerating agent, a guanidine, aldehyde - amine, ~~aldehyde~~ - ammonia, ~~thiazole~~ ^{thiazole}, sulfonamide, thiourea, thiuram, dithiocarbamate, ~~xanthate accelerating agent~~ is used.

Another coating method using the binder polymer is exemplified by a method in which a mixture of the large ring compound and the binder polymer is applied, and then radial rays, electron rays or ultraviolet rays are applied to cause the applied material to be crosslinked.

As a method for covering the negative pole activating material pole by the electrolytic polymerization, a monomer, such as dibenzocrown ether, is mixed in the electrolytic solution, and then the electrolytic polymerization is performed while using the negative pole activating material or the conductive matrix as an anode. The solvent of the electrolytic solution is exemplified by ~~acetonitrile~~ ^{acetonitrile} (CH₃CN), ~~benzonitrile~~ ^{benzonitrile} (C₆H₅CN), propylene carbonate (PC), dimethylformamide (DMF), tetrahydrofuran (THF),

- 1 nitrobenzene ($C_6H_5NO_2$), dichloroethane, diethoxyethane, chlorobenzene, γ - butyrolactone and dioxolan^e and their mixture^f. It is preferable that the solvent be dehydrated with active alumina, molecular ~~sheave~~^{sieve},
5 phosphorus pentaoxide or calcium chloride. As an alternative to this, it is preferable, depending upon the type of ~~the~~^{the} solvent^g that the solvent be distilled ~~under~~^{in the} presence of alkaline metal in inactive gas to remove impurities and to be dehydrated. The supporting
10 electrolyte is an acid, such as H_2SO_4 , HCl or HNO_3 or salt composed of monovalent metal ion (Li^+ , K^+ , Na^+ , Rb^+ or Ag^+) or tetraammonia ion (tetrabutyl ammonia ion (TBA^+) and tetraethyl ammonia ion (TEA^+)) and Lewis acid ion (BF_4^- , PF_6^- , AsF_6^- or ClO_4^-). It is preferable that
15 the foregoing salt is refined by re-crystallization or ~~it is~~^{it is} heated under lowered pressure to sufficiently dehydrate and deoxidize the salt.

As the monomer, crown ether/benzo - 15 - crown - 5, crown ether/benzo - 18 - crown - 6, crown ether/N -
20 phenylaza - 15 - crown - 5, crown ether/dibenzo - 18 - crown - 6, crown ether/dibenzopyridino - 18 - crown - 6, crown ether/dibenzo - 24 - crown - 8, 1, 13 - bis (8 - quinolyl) - 1, 4, 7, 10, 13 - ~~penta~~^{penta oxalide cone} ~~oxatridecan~~, 5, 6 - benzo - 4, 7, 13, 16, 21, 24 - hexaoxa - 1, 10 -
25 diazabicyclo [8. 8. 8] - ~~hexakosan~~^{hexacosan}, 5, 6 - 14, 15 - dibenzo - 4, 7, 13, 16, 21, 24 - hexaoxa - 1, 10 -
diazabicyclo [8. 8. 8] - ~~hexakosan~~^{hexacosan}, bis [(benzo - 15 -

- 1 crown - 5 -) - 15 - ^{ylmethyl} ~~ilmethyl~~] pimelate, crown
ether/dibenzo - 30 - crown - 10, N, N' - dibenzyl - 1,
4, 10, 13 - tetraoxa - 7, 16 - ^{diazocyclooctadecane} ~~diazacyclooctadecan,~~
dilithiumphthalocyanin^l, 4' - nitrobenzo - 15 - crown -
5 5, 3, 6, 9, 14 - tetrathiabicyclo [9. 2. 1] tetradeca -
11, 13 - diene and their mixtures

Since the performance of the battery deteriorates if the polymer film for covering the surface of the negative pole activating material is dissolved in the electrolytic solution, it is preferable to be crosslinked.

- It is preferable that the thickness of the film to be formed on the surface of lithium ranges from 50 Å to 100 ^{μm} further preferably ranges from 100 Å to 10 μ.
- 15 The optimum thickness of the film differs depending upon the density or the ^{porosity} ~~void ratio~~ of the film and considerably differs depending upon the type of the electrolytic solution. The thickness of the film can be adjusted by changing the concentration of the main
- 20 material in the coating liquid for forming the film.
6. Polymer (polyphosphazene) Film in Which Phosphor Atoms and Nitrogen Atoms are Alternately Bonded in a Phosphor-Nitrogen Double Bond Manner

The surface of the negative pole activating material is covered with a polymer (polyphosphazene) film through which ions for use in the reactions in the battery can be passed and in which phosphor atoms and

1 nitrogen atoms are alternately phosphor-nitrogen double
bonded. As a result, lithium and the electrolytic
solution do not come in contact with each other if the
negative pole activating material is lithium.

5 Therefore, formation of the polymer film from the
solvent of the electrolytic solution on the surface of
lithium can be prevented. If the negative pole
activating material is zinc, elution of zinc into the
electrolytic solution can be prevented. As a result,
10 formation of dendrites can be prevented, and therefore
the life against ^{the} charge and discharge cycle can be
lengthened.

Since the lithium battery according to the
present invention comprises ^{a flame retardant} ~~the~~ polyphosphazene film
15 covering lithium ~~is a flame retardant film,~~ safety
against emergency breakage can be improved.

The polymer for use as the covering material
can be obtained by heating a dichloropolyphosphazene
trimer to 200 to 300°C and by ring-opening
20 polymerization. The dichloropolyphosphazene trimer can
be synthesized from phosphorus pentachloride and ammonia
chloride or ammonia. Any one of the following ^{catalysts} ~~catalyzer~~
is used at the time of the polymerization: benzoic
acid, sodium benzonate, 2, 6 - di - p - cresol, water,
25 methanol, ethanol, nitromethane, ether, heteropoly acid,
sulfur, zinc, tin and sodium. Further, various types of
polyorganophosphazene can be obtained by substituting

1 chloride atoms of polydichlorophosphazene by an organic reagent or an organic metal reagent.

If the surface of lithium is coated with the foregoing polymer solution, it is preferable that the polymer solution ^{be} dehydrated and deoxidized sufficiently ^{sufficiently dehydrated} and ~~be used in inactive gas dehydrated sufficiently~~ (however, the necessity of strictly controlling water can be eliminated when the polymer is previously applied to the conductive matrix or when the negative pole activating material is zinc).

It is preferable to use a solvent in the foregoing solution which has been dehydrated with active alumina, molecular ^{sieve} ~~sheave~~, phosphorus pentaoxide ^{or} calcium chloride. As an alternative to this, it is preferable, depending upon the type of ^{the} solvent, that the solvent be distilled ^{in the} ~~under~~ presence of alkaline metal in inactive gas to remove impurities and to be dehydrated (however, the necessity of strictly controlling water can be eliminated when the polymer is previously applied to the conductive matrix or when the negative pole activating material is zinc).

An electrolyte may previously be mixed when the foregoing film is formed. ~~It leads to a fact that~~ Wettability between the electrolytic solution and the film can be improved ^{in this way}, causing ions to easily pass through the film. In order to facilitate the ^{transfer} ~~movement~~ of ^{the} charge at the time of charging, conductive

- 1 powder, such as carbon or titanium, fiber or whisker
may be mixed at the time of forming the film.

Since the performance of the battery deteriorates
if the polymer coating film is dissolved in an organic
5 solvent of the electrolyte, it is preferable to be
crosslinked in such a manner, for example, ultraviolet
rays, electron rays or radial rays are applied or a
crosslinking material, such as a radical generating
agent, is used.

- 10 It is preferable that the thickness of the film
to be formed on the surface of the negative pole
activating material ranges from 50 Å to 100 μ^{and} more
preferably ranges from 100 Å to 10 μ.

- The optimum thickness of the film differs
15 depending upon the density or the ^{porosity} ~~void~~ ratio of the
film and considerably differs depending upon the type
of the electrolytic solution. The thickness of the film
can be adjusted by changing the concentration of the
main material in the coating liquid for forming the
20 film.

7. Other Organic Polymer Film

- The surface of the negative pole is covered with
an organic polymer containing one or more types of
elements selected from a group consisting of oxygen,
25 nitrogen and sulfur and permitting ions relating the
battery reactions to pass through. The direct contact
of fresh negative active materials precipitated during

1 the charging reactions can be prevented due to the
foregoing cover film. Therefore, the negative pole is
not covered with a substance prepared due to the
reactions with the electrolytic solution and having low
5 conductivity. As a result, the growth of dendrites can
be prevented.

The organic polymer containing oxygen is
exemplified by cellulose, alkyl cellulose,
nitrocellulose, acetyl cellulose, chitin, chitosan,
10 polyethylene glycol, polyethylene oxide, polypropylene
oxide, polyvinyl alcohol, polyvinyl acetate,
polylactide, polylactone, poly - 3 - hydroxyalcanoate,
polyglycol acid, polyacetic acid, ^{polydioxanone} ~~polydioxanon~~, glycol
acid - lactone copolymer, polyethylene terephthalate,
15 polyphenylene oxide, polyether etherketone and the like.
It is preferable to use acetyl cellulose, chitin or
polyvinyl alcohol.

The organic polymer containing nitrogen is
exemplified by collagen, chitin, chitosan, polyurethane,
20 polyimide, polyether imide and the like.

The organic polymer containing sulfur is
exemplified by polyphenylene sulfide, ^{polysulfone} ~~polysulfon~~ and
polyether ^{sulfone} ~~sulfon~~.

The negative pole is covered with the foregoing
25 organic polymer film formed in such a manner that the
solution of the organic polymer is applied and dried and
then ~~a~~ crosslinking reactions are ^{performed} ~~caused to occur~~.

- 1 Another method of forming the film may be employed in
such a manner that the organic polymer is used as a
target in a sputtering method. Another method may be
employed in which a monomer serving as the organic
5 polymer is plasma-polymerized to form the film.

The application may be completed by dipping,
spraying or screen printing.

- The crosslinking reactions can be performed by
any one of the following methods: irradiation of
10 ultraviolet rays, electron rays or radial rays; or
decomposition of a radical generating material such as
azobis¹⁵⁰buty^{re}lonitr^{yl}le or peroxy benzoyl. The reason why
the organic polymer of the film is crosslinked is that
elution of the film into the electrolytic solution must
15 be prevented.

- The thickness of the film must range so far as
ions in the electrolytic solution relating to the
battery reactions are able to pass through the same.
It differs depending upon the material and the void ^{porosity}
20 ~~ratio~~ ^{of} of the film and the type of the ion. It is
preferable that the mean thickness ranges from 10 Å
to 100 ^{and} ~~more~~ preferably ^{from} 100 Å to 10 μ. If the ion
permeability through the film is unsatisfactory, an
electrolyte may be mixed at the time of forming the
25 film.

If the electrolytic solution of the battery is
a water soluble solution and it is not hydrophilic, it

1 is preferable to perform a treatment using a silane
coupling material or a titanate coupling material to
attain hydrophilic characteristics.

Although the various covering materials and
5 coating methods have been described ^{with respect to directly covering} while employing the
negative pole activating material ~~is directly covered~~
with the film, another method may be employed in which
the conductive matrix is ~~previously~~ covered with the
coating material and then the negative pole activating
10 material is introduced.

Negative Pole Activating Material

As the negative pole activating material 101,
lithium, lithium alloy, zinc or zinc alloy is used. The
lithium alloy may contain one or more types of elements
15 selected from ^{the} a group consisting of magnesium, aluminum,
titanium, tin, indium, boron, gallium, potassium,
sodium, calcium, zinc, ^{and} lead and the like. The zinc
alloy may containing one or more types of elements
selected from a group consisting of aluminum, indium,
20 magnesium, tin, titanium, copper, lead, tin, lithium, ^{and}
mercury and the like.

The negative pole activating material for the
alkali-zinc battery may be zinc, zinc alloy, zinc oxide
or zinc hydroxide, the negative pole activating material
25 being uniformly kneaded with a bonding material or a
kneading solution to obtain paste. The paste is applied
to a collector followed by drying, ~~them~~ so that a negative

1 plate is obtained.

The ^{binding} ~~bonding~~ material is exemplified by polyvinyl alcohol, a cellulose material such as methyl cellulose or carboxymethyl cellulose, a polyolefin material such as polyethylene, a fluoro-resin such as polytetrafluoroethylene and a polyamide resin such as nylon.

The kneading solution may be an organic solvent such as ethylene glycol or water containing oxo acid salt such as sodium phosphate or the like.

The collector may be an iron plate applied with nickel plating and having apertures, a foam metal, ~~or~~ nickel mesh or the like.

Positive Pole

The positive pole is formed by mixing a positive pole activating material, conductive powder and a ^{binding} ~~bonding~~ material on the collector. In order to easily form the positive pole activating material, a solvent-resisting resin, such as polypropylene or polyethylene or fluoro-resin is used as the ^{binding} ~~bonding~~ material if necessary. In order to further easily collect electric currents, the conductive powder is mixed at the time of ~~the~~ formation. The material of the conductive powder is exemplified by ~~various~~ ^{various} carbon, copper, nickel, ~~and~~ titanium and the like.

Positive Pole for Lithium Secondary Battery

The positive pole activating material 104 of the

1 lithium secondary battery is made of a compound having
layers through which lithium ions can be passed, the
compound being a transition metal such as a metal oxide
exemplified by manganese oxide, vanadium oxide,
5 molybdenum oxide, chrome oxide, cobalt oxide, nickel
oxide, titanium oxide, iron oxide, and tungsten oxide
or a metal sulfide exemplified by titanium sulfide,
molybdenum sulfide, iron sulfide and shebrell phase
sulfide ($\text{MyMo}_6\text{S}_{8-2}$ (M: metal such as copper, cobalt or
10 nickel)). The transition metal element may be an
element having partially shell d or shell f. The
metal selenide is exemplified by niobium selenide.
The metal hydroxide is exemplified by oxyhydroxide. The
conductive polymer is exemplified by polyacetylene,
15 polyparaphenylene, polyaniline, polythiophene, polypyrrole
and polytriphenylamine. The composite oxide is
exemplified by $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ and $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$.

The positive pole is manufactured in such a manner that paste obtained by adding a ^{binding} ~~bonding~~ material, such as polyethylene, polypropylene or a fluororesin, to the positive pole activating material 104 is pressed against the positive pole collector 103. In order to improve the collecting performance of the positive pole, it is preferable to add conductive powder to the paste.

25 The conductive powder may be a carbon material
such as acetylene black or metal such as copper, nickel
or titanium. The collector 103 may be fiber-like, porous

- 1 or mesh-shape carbon material, stainless steel,
titanium, nickel, copper, platinum or gold.

Positive Pole for Nickel-Zinc Battery

- 5 The positive pole of the nickel-zinc battery is *either*
~~categorized to~~ a paste type pole formed by directly
charging nickel hydroxide powder into the collector *and or*
a sintering type formed by immersing nickel hydroxide
into *a* small apertures of the nickel sintered plate.

- 10 The paste type positive pole is formed in such a
manner that paste obtained by uniformly kneading an
additive, such as nickel or cobalt, with a ~~binding~~ *binding*
material or a kneading solution is applied to the
collector followed by drying them.

- 15 The ~~binding~~ *binding* material and the collector are made
of materials of the same type as those of the zinc
negative pole.

- 20 The sintered type positive pole is manufactured
in such a manner that a sintered plate obtained by
sintering nickel powder on the nickel-plated iron plate
having apertures is immersed in a mixed solution of
nickel salt serving as a main active material and
cobalt salt serving as an additive and then ~~caused to~~
reacted with an alkali solution of, for example, sodium
hydride so that nickel hydroxide is impregnated into
25 the sintered plate.

Positive Pole for Air-Zinc Secondary Battery

The positive pole of the air-zinc secondary

- 1 battery is made of a material composed of an air pole,
a water-repellent film and a diffuser paper sheet.

The ^{catalyst}~~catalyzer~~ of the air pole is prepared in such
a manner that silver, manganese dioxide, nickel-cobalt
5 composite oxide or platinum is added to a carbon
material, such as porous carbon (active carbon) or
carbon black, porous nickel, copper oxide or the like
having a specific area of 200 to 1000 m²/g.

The water-repellent film is provided to prevent
10 leakage of the electrolytic solution passed through the
air pole to the outside of the battery. The water-
repellent film is made of a fluoro-resin such as
polytetrafluoroethylene. The diffuser paper sheet is
provided for the purpose of uniformly supplying oxygen
15 to the overall surface of the air pole, the diffuser
paper sheet being made of cellophane or the like.

A zinc-bromine battery comprising the negative
pole activating material which is zinc includes bromine
to serve as the positive pole activating material.

20 Coating of Positive Pole

In order to prevent generation of dendrites, which
causing ~~the~~ short circuit, ⁱⁿ at the time of ~~the~~ charge, the
surface of the positive pole is covered with a film
through which ions for use in the reactions in the
25 battery can be passed, so that the life of the battery
against the cyclic usage can be lengthened.

The coating material may be a polymer of the

1 derivative of a large ring compound, a polymer of the
derivative of an aromatic hydrocarbon, fluororesin,
silicon resin, titanium resin, polyolefin, inorganic
oxide, nitride, carbide or halide. It is effective to
5 improve the safety of the lithium secondary battery to
cover the positive pole with a flame retardant or non-
combustible material, such as fluororesin,
polyphosphazene, an inorganic oxide, nitride, carbide
or halide.

10 If the film through which ions for use in the
reactions in the battery can be passed is a multi-layer
metal oxide film formed by using a bimolecular film as a
mold, ⁱⁿ ~~an~~ effect ^{of} a separator can be obtained and ~~an~~ ^{ing can be prevented}
~~effect of preventing the short circuit~~ between the
15 negative pole and the positive pole ~~can further be~~
~~improved.~~

Electrolyte

20 The electrolyte is used as it is or in the form
of a solution in which it is dissolved in a solvent or
after it has been solidified by adding a gelatinizing
material, such as a polymer, to the solution. Generally
an electrolytic solution ^{AV}, in which the electrolyte is
dissolved in a solvent, is held in a porous separator.

25 The conductance of the electrolyte must be raised
as much as possible because it relates to the internal
resistance of the battery and considerably affects the
current density at the time of the charge and the

- 1 discharge. It is preferable that the conductance at
25°C be 1×10^{-3} S/cm or higher, more preferably $5 \times$
 10^{-3} S/cm or higher. x

- In a Case Where Negative Pole Activating Material is
5 Lithium or Lithium Alloy

- The electrolyte is made of an acid, such as
 H_2SO_4 , HCl or HNO_3 , a salt composed of Lewis acid ion
(BF_4^- , PF_6^- , AsF_6^- or ClO_4^-) or their mixture. Further,
positive ions, such as sodium ions, potassium ions,
10 tetraalkylammonium ions, and the Lewis acid ions may be
used together. It is preferable that the foregoing salt
is heated under lowered pressure to sufficiently
dehydrate and deoxidize the salt.

- The solvent of the electrolyte is exemplified by
15 acetonitrile (CH_3CN), benzonitrile (C_6H_5CN), propylene
carbonate (PC), ethylene carbonate (EC), dimethyl
formamide (DMF), tetrahydrofuran (THF), nitrobenzene
($C_6H_5NO_2$), dichloroethane, diethoxyethane, chlorobenzene,
n/e γ -butyrolactone, dioxolane, sulfolane, nitromethane,
t/e
20 dimethylsulfide, dimethylsulfoxide, dimethoxyethane,
f
methyl formate, 3-methyl-2-oxazolidinone, 2-
methyltetrahydrofuran, sulfur dioxide, phosphoryl
chloride, thionyl chloride, sulfonyl chloride, dimethyl
formaldehyde, γ -butyrolactone, and tetrahydrofuran and
l/y 25 their mixture.

It is preferable that the foregoing solvent be
dehydrated with active alumina, molecular sieve,

siwe

- 1 phosphorus pentaoxide or calcium chloride. As an
alternative to this, it is preferable depending upon the
type of the solvent that the solvent be distilled under
presence of alkaline metal in inactive gas to remove
5 impurities and to be dehydrated.

It is preferable to gel the electrolytic solution
to prevent leakage of the electrolytic solution. As the
gelling material, it is preferable to use a polymer of a
type which swells when it absorbs the solvent of the
10 electrolytic solution, the gelling material being a
polymer exemplified by a polyethylene oxide, polyvinyl
alcohol and an polyacryl amide..

COPIED FROM ORIGINAL
{In a Case Where the Negative Pole Activating Material
is Zinc or Zinc Alloy}

- 15 As the electrolytic solution, salt of alkali or
zinc borate is used which is a sole or a mixed solution
of potassium hydroxide, sodium hydroxide, lithium
hydroxide or ammonium hydroxide.

It is preferable to gel the electrolytic solution
20 to prevent leakage of the electrolytic solution. As the
gelling material, it is preferable to use a polymer of a
type which swells when it absorbs the solvent of the
electrolytic solution, the gelling material being a
polymer exemplified by a polyethylene oxide, polyvinyl
25 alcohol and an polyacryl amide.

the
In a case of a battery such as a bromine - zinc
battery except for the alkali battery, a salt such as

1 zinc borate is used.

The solid electrolyte is manufactured in such a manner that a polymer compound of a polyethylene oxide (PEO) type and salt of the electrolyte are dissolved in
5 the foregoing non-water-soluble solvent to be gelled and then they are developed on, for example, a flat board to evaporate the non-water-soluble solvent. The PEO polymer compound is exemplified by polyethylene oxide or a poly (methoxyethoxyphosphazene) crosslinked by
10 polyethylene oxide or isocyanate.

The electrolytic solution for the alkali-zinc secondary battery may be a solution of sodium hydroxide, potassium hydroxide or lithium hydroxide or their mixture.

15 Separator

The separators (108, 208 and 308) are provided to prevent short circuits between the positive pole and the negative pole. They also act to hold the electrolytic solution.

20 The separator must meet the following conditions. (C) (D)

(1) The separator cannot be dissolved in the electrolytic solution and must be stable with respect to the same.

(2) The separator is able to absorb a large
25 quantity of the electrolytic solution and must exhibit satisfactory holding force.

(3) The separator must have small apertures

1 through which lithium ions and hydroxide ions can be
passed.

(4) The separator must have small apertures each
having a size which is able to prevent the penetration
5 of dendrite.

(5) The separator must be mechanically strong so
as not to be broken or deformed excessively when it is
wound.

The material that is able to meet the foregoing
10 conditions is exemplified by a unwoven fabric or a
micropore structure of glass, polypropylene,
polyethylene, or fluororesin.

Also a metal oxide film having small apertures or
a resin film formed by combining metal oxides may be
15 used. If a metal oxide film in the form of a multi-
layer structure is used, dendrite cannot easily pass
through it and therefore an effect of preventing the
short circuits can be obtained. If a fluororesin film
which is a flame retardant or a glass or a metal oxide
20 film which is a noncombustible material is used, the
safety can further be improved.

Since the electrolytic solution of the alkali-
zinc secondary battery is a water-type solvent, a
hydrophilic separator must be used which is exemplified
25 by a non-woven fabric or a micropore structure of nylon,
polypropylene or hydrophilic polypropylene.

1 Collector

Collectors 100, 103, 200 and 300 are made of fiber, porous or mesh-like carbon, stainless steel, titanium, nickel, copper, platinum or gold.

5 Shape and Structure of Battery

The battery is formed into a flat, cylindrical, square (rectangular) or a sheet shape battery. The spiral and cylindrical structure is enabled to have a large electrode area by winding while interposing the separator between the negative pole and the positive pole so that a large electric current can be caused to flow at the time of the charge and the discharge. The rectangular type battery enables an accommodation space for accommodating the secondary battery to be used effectively. The structure may be a single-layer structure and a multi-layer structure.

Figs. 2 and 3 illustrate the schematic cross-sectional views which respectively illustrate an example of a single-layer flat battery and a spiral and cylindrical battery. Referring to Figs. 2 and 3, reference numeral 201 and 301 represent negative poles covered with films, and 200 and 300 represent collectors for the negative poles 201 and 301. Reference numeral 203 and 303 represent positive pole made of the positive pole activating material. Reference numeral 304 represents a collector for the positive pole, and 206 and 306 represent negative terminals (caps for the

1 negative poles 201 and 301). Reference numeral 207 and
307 represent outer cases (cases serving as positive
pole cases and battery cases), 208 and 308 represent
separators which hold the electrolytic solution, 210 and
5 310 represent insulating packings, and 311 represents an
insulating plate.

Referring to Fig. 5, reference numeral ~~5201~~ and
X 5301 represent ⁹lithium members subjected to surface
treatment. In the structure shown in Fig. 5, reference
10 numeral 201 and 310 represent lithium members subjected
to surface treatment.

The batteries shown in Figs. 2 and 3 are
manufactured in such a manner that the separators 208
and 308 are held between the negative poles 201, ~~301~~
15 subjected to the surface treatment and the positive
poles 203 and 303 to be placed in the positive pole
cases 207 and 307 followed by injecting the electrolytic
solution. Then, the negative pole caps 206, 306, the
insulating packing, 210 and 310 are assembled so that the
20 batteries are manufactured.

In the case of the lithium battery, it is
preferable that the preparation of the material and
assembling of the battery are performed in dry air from
which water has sufficiently been removed or in a dry
25 inactive gas.

Battery Case (Outer Case)

The battery case may be a metal outer case also

5102

3

en

- 1 serving as an output terminal or a plastic resin case.

The positive pole cases 207, 307, the negative pole caps 206 and 306 are made of stainless steel¹, and in particular, titanium clad stainless steel or copper clad stainless steel or a steel plate applied with nickel-plating.

Although the structures shown in Figs. 2 and 3 comprises the positive pole cases 207 and 307^{then} also ~~representing~~ serving as the battery cases and the output terminals.

- 10 The battery case may be made of metal such as aluminum or zinc, plastic such as polypropylene or a composite material of metal, glass fiber and plastic as well as the stainless steel.

Insulating Packing

- 15 The insulating packings 210 and 310 may be made of fluoro-resin, polyamide resin, polysulfon resin or rubber.

Cap

- 20 The capping method may be a bonding method, welding method, soldering method or a glass sealing method as well as a caulking method using a gasket such as an insulating packing.

Insulating Plate

- 25 The insulating plate 311 for insulating the inside of the battery may be made of an organic resin or ceramics.

1

5

10

15

20

25

5

5

5

5

[illegible]

15

20

AD

1 chlorine, hydrogen fluoride, hydrogen chloride or
chloride trifluoride be diluted with inactive gas such
as argon gas or helium gas.

The nitrogen compound and the halogen compound may
5 be mixed with each other or contain oxygen gas, hydrogen
gas, argon gas, helium gas, xenon gas or the like added
thereto to improve the activity of the reactive gas or
to control the activity. The negative pole may be
treated with plasma of hydrogen gas or argon gas prior
10 to treating the surface of the negative pole so that a
fresh negative pole surface is caused to appear.

More specifically, according to the present
invention, there is provide a secondary battery
manufactured in such a manner that active nitrogen
15 plasma or fluorine plasma or hydrogen fluoride is
brought into contact with the surface of lithium to
cause reactions to take place, an inactive thin film
made of lithium nitride or lithium fluoride and allowing
lithium ions to pass through is formed on the surface of
20 lithium, and the lithium portion is used as the negative
pole. As a result, the direct contact of lithium
precipitated at the time of the charge with the
electrolytic solution is prevented so that the
generation of dendrite~~y~~ at the time of the charge is
25 prevented. Therefore, a lithium battery exhibiting a
long life against the charge and discharge cycle can be
obtained. Further, the application of the foregoing

1 treatment to the surface of lithium prevents the
reactions between lithium and water. Further, handling
can be made easier.

It is preferable that the thickness of the
5 treatment layer to be formed on the surface of lithium
ranges from 10 Å to 1 μ, more preferably 50 Å to 1000 Å.
The thickness is adjusted by the reaction time or the
concentration of the reaction gas.

It is preferable that the concentration of nitrogen
10 atoms or halogen atoms in the treatment layer formed on
the surface of lithium be gradually lowered from the
surface to the inside portion of lithium.

Positive Pole Activating Material


The positive pole activating material 5104 may be
15 a material into which lithium can be introduced into the
interlayer thereof, the material being exemplified by a
metal oxide such as a nickel oxide, cobalt oxide,
titanium oxide, iron oxide, vanadium oxide, manganese
oxide, molybdenum oxide, chrome oxide or tungsten oxide,
20 or a metal sulfide such as molybdenum sulfide, iron
sulfide or titanium sulfide, a hydroxide such as oxy
iron hydroxide, or a conductive polymer such as
polyacetylene, polyaniline, polypyrrole or polythiophene.

In order to make easier the formation of the
25 positive pole activating material, solvent-resisting
resin, such as polypropylene, polyethylene or
fluororesin is used as a bonding material if necessary.

1 In order to further facilitate collection of electric
current, it is preferable to mix conductive powder at
the time of molding the positive active material. The
conductive powder may be carbon black, copper, nickel or
5 titanium.

Fig. 8 illustrates an example *of* a pattern of
stacked layers according to the present invention in
which a conductive layer, a semiconductor layer and an
insulating layer are formed between the negative pole
10 and the separator. Referring to Fig. 8, reference
numeral 001 represents a negative pole, 002 represents a
dendrite, 003 represents the conductive layer or the
semiconductor layer, 004 represents a separator, 005
represents an insulating layer, 006 represents an
15 electrolytic solution, and 007 represents a positive
pole.

Fig. 8 is a schematic view which illustrates an
effect of the present invention in an example in which
the insulating layer through which lithium ions can be
20 passed and a conductive layer are stacked on the surface
of the lithium negative pole.

 *In* ~~When~~ the charging mode, lithium (or zinc) is
precipitated on to the negative pole 001. At this time,
a portion in which the current density is high is
25 locally generated on the negative pole 001 depending
upon the projections and pits of the surface and upon
the thickness of the insulating film. Lithium (or zinc)

deposited
at

1 is selectively precipitated, causing the dendrite 002 to grow. With proceeding of the charging or discharging cycle, the dendrite 002 reach the conductive layer 003. When a short circuit state between the dendrite 002
5 and the conductive layer 003 is realized, the current density at the negative pole is lowered at the time of the charge. Therefore, the further growth of the dendrite 002 is prevented, and therefore penetration of the dendrite 002 through the separator 004 to reach the
10 positive pole 007 can be prevented.

By covering the negative pole with the ion permeable insulating layer 005, active lithium (or zinc) precipitated at the time of the charge cannot easily react with the electrolytic solution. Therefore, the
15 generation of the growth of the insulating film can be prevented.

Figs. 9A to 9H illustrate various examples in which one or more types of layers selected from the ion permeable conductor, semiconductor and insulating
20 material are formed between the negative pole and the separator. Reference numerals shown in Figs. 9A to 9H are the same as those shown in Fig. 8. The present invention is not limited to the structure shown in Figs. 9A to 9H.

It is preferable that the conductive layer to be
25 formed between the negative pole and the separator be made of carbon, Ni, Ti, Pt, Al, Pb, Cr, Cu, V, Mo, W, Fe, Co, Zn or Mg, more preferably made of carbon, Ni

1 or Ti.

If the semiconductor layer is formed in place of the conductive layer, a similar effect obtainable from the conductive layer can be obtained. If the semiconductor layer is employed, the current density at the time of the growth of dendrite is higher than that in the case where the conductive layer is formed.

However, the conductivity is lowered as compared with the case where the conductive layer is formed. Therefore, an advantage can be realized that the easy conduction with the positive pole is prevented.

The semiconductor layer may be made of diamond, Si, nickel oxide, copper oxide, manganese oxide, titanium oxide, zinc oxide, zirconium oxide, tungsten oxide, molybdenum oxide or vanadium oxide.

The insulating layer may be made of a halide such as lithium fluoride or magnesium fluoride, a nitride such as silicon nitride, a carbon such as silicon carbide, or a polymer such as polyethylene, polypropylene or fluororesin.

The forming method and materials of the conductive layer, the semiconductor layer, the insulating layer and the composite layer will now be described. When lithium is used, the following two desires must be met.

If water is left in the raw material, water and lithium react with each other. Therefore, water must be previously removed by a method by dehydration using

conditions

- sieve*
- 1 active alumina, molecular sheave, phosphorus pentaoxide
or calcium chloride. If a solvent is used, it is
sometimes preferable that the solvent be distilled under *in the*
presence of alkaline metal in inactive gas to remove
5 impurities and to be dehydrated.

The temperature at which the foregoing layer is applied to the surface of the negative pole must be lower than a level at which the negative pole activating material is melted.

10 Conductive Layer

As a typical example of the conductive layer, manufacturing method of carbon conductive layer or a metal conductive layer made of, for example, Ni or Ti, will now be described.

15 Carbon

- The form of the carbon crystal is categorized to crystal, amorphous, and a mixture of them. The carbon to be applied may be carbon powder or carbon fiber or a carbon paper sheet or the like obtainable by paper
20 machining.

The surface of the negative pole can be covered with carbon by any one of the following methods.

- (1) A solution obtained by uniformly dispersing carbon powder or carbon fiber in an organic solvent such
25 as toluene or xylene is, under inactive atmosphere of Ar, is applied to the surface of the negative pole by a spraying method, screen printing method, a coater method
- X*
- ③*

1 or a dipping method followed by drying the solution, and
then carbon are pressed against the surface.

(2) The carbon paper is stacked on the surface of the
negative pole, and then the carbon is pressed against
5 the surface.

(3) A vacuum evaporation method such as sputtering
using carbon as the target is performed so that the
surface of the negative pole is covered with carbon.

(4) A CVD (Chemical Vapor Deposition) method is
10 performed under the presence of an organic compound
which is the raw material of carbon so that the negative
pole is covered with carbon.

In the foregoing coating method, the carbon powder
or the carbon fiber must be pressed against the surface
15 so that the contact is improved. The pressing work is
performed by using a pressing machine or a roller press.
The temperature at the time of the pressing work must be
lower than a level at which the negative pole activating
material is melted. It is preferable that the thickness
20 of the coating range from 10 to 100 μm , more preferably
from 50 μm or thinner in order to prevent reduction of
the quantity of the contained negative pole activating
material.

The pressing method to be performed after the
25 carbon paper has been stacked may be a method using a
pressing machine or a roller press, a method in which
the positive pole plate and the negative pole plate are

1 wound while interposing the separator, and a method in
which winding pressure or stacking pressure is applied
while interposing the carbon paper at the time of
stacking the carbon paper. The latter method is able to
5 eliminate a process of previously pressing the carbon
paper against the negative pole and the carbon paper can
be pressed in the winding or the stacking process. It
is preferable that the carbon paper having a thickness
ranging from 150 to 300 μm be pressed to have a
10 thickness ranging from 75 to 150 μm .

The sputtering coating method is performed in such
a manner that carbon is used as the target in an
inactive atmosphere of argon and DC or RF discharge is
performed so that the surface of the negative pole is
15 covered with carbon.

The raw material of the CVD carbon coating method
may be saturated hydrocarbon such as methane,
unsaturated hydrocarbon such as acetylene, ethylene,
propylene or benzene, carbon monoxide, alcohol or
20 acetone. The exciting method is exemplified by a method
using plasma, laser or heating filament. It is
preferable that the thickness of the carbon applied be 1
 μm or thinner, more preferably 1000 \AA .

In the case of the plasma CVD method, the power
25 source for the glow discharge may be a high frequency or
a DC power source. The high frequency source may be a
usual band source such as radio frequency (RF), VHF or

1 microwave source. The wavelength of the radio waves is
typified by 13.56 MHz, while that of the microwave is
typified by 2.45 GHz.

C 5 If the laser CVD is employed, an ultraviolet ArF
excimer laser or infrared ray CO₂ is used as the laser
beam source.

Metal Such as Ni or Ti

The metal such as Ni or Ti is applied to the
surface of the negative pole by a sputtering method as
10 is employed to apply carbon, a CVD method, an electron
beam evaporation method or a cluster ion beam
evaporation method.

The target for use in the sputtering method may be
Ni or Ti or the like. When a composite film is formed,
15 two or more kinds of targets are used; to perform either
or both of the targets are subjected to the sputtering
process. The sputtering method must be performed under
an inactive atmosphere of argon similarly to carbon.

The CVD coating method employs the following
20 materials as the raw materials.

As the raw material for Ni and Ti, a solution in
which organic metal such as acetylacetone complex of
nickel (or titanium) is dissolved in non-water-soluble
solvent such as hexane, acetone or toluene or a solution
25 in which a halide such as nickel chloride (or titanium)
is dissolved in a non-water-soluble solvent such as
ethanol is subjected to bubbling in a carrier gas

1 (hydrogen or the like) and then the solution is
introduced into the CVD reaction chamber to cause the
CVD reactions to take place so that coating is
performed.

5 When a composite film of Ni and carbon is formed, a
hydrocarbon such as methane is used together with a
metal compound.

Semiconductor Layer

The semiconductor layer is exemplified by diamond,
10 Si, nickel oxide, copper oxide, cobalt oxide, manganese
oxide, titanium oxide, zinc oxide, zirconium oxide,
tungsten oxide, molybdenum oxide, or vanadium oxide. The
coating method may be a sputtering method, an electron
beam evaporation method, a plasma CVD method, a light
15 CVD method, a laser CVD method or a heat CVD method.

Si

As the target for use in the sputtering method, Si
or the like is used.

In the CVD method, the raw material for Si may be
20 hydroxide gas such as SiH_4 or Si_2H_6 , fluorine gas such as
 SiHF_3 , SiH_2F_2 or SiH_3F , or a chlorine gas such as SiHCl_3 ,
 SiH_2Cl_2 or SiHCl_3 . If the foregoing raw material is in
the form of liquid, it is heated as to be in the form of
vapor or subjected to bubbling by a carrier gas before
25 it is introduced. If a composite film of Si and carbon
material is formed, hydrocarbon such as methane is used
together with the foregoing gas. A compound comprising

TELETYPE

a/so

a

1 carbon, P or B may be adequately mixed.

Oxide such as Nickel Oxide and Titanium Oxide

The nickel oxide and titanium oxide can be prepared by a sol-gel method in which alkoxide such as nickel or
5 titanium or organic metal is dissolved in alcohol and then it is hydrolyzed, an anodic oxidation method in which a solution in which nickel salt or titanium salt is dissolved is electrolyzed, or a CVD method or an electron beam evaporation method to introduce oxygen gas
10 into the reaction chamber.

Insulating Layer

As the insulating layer, a halide, a nitride, a carbide or resin such as polyethylene (PE), polypropylene (PP) or fluororesin is used. As the coating method, a
15 sputtering method, a plasma CVD method or a coating method is used.

Other resins may be used such that a resin obtained by gasifying a monomer of an organic polymer and by plasma polymerizing it or a resin obtained by sputtering
20 an organic polymer or a film of an organic polymer may be used. In this case, the resin member must have small aperture through which ions can be passed and must not react with the electrolytic solution.

Nitride

25 In the sputtering method, a target comprising nitride exemplified by silicon nitride or lithium nitride is used. As an alternative to this, Si or Li is

1 used as the target, nitrogen gas or ammonia is used as
the reaction gas and sputtering is performed in the
foregoing state.

PE and PP

5 In the plasma CVD method, SiH_4 or Si_2H_6 and
ammonia, nitrogen gas or NF_3 are used together as the
raw materials.

In the sputtering method, a PE or PP target is
used to perform sputtering to cover the insulating
10 layer.

In the plasma polymerization method, ethylene is
used as the raw material in the case of PE, while
propylene is used in the case of PP.

Fluororesin

15 In the sputtering method, the target comprises a
polymer or a copolymer such as polytetrafluoroethylene,
polytrifluoroethylene, vinyl fluoride, vinylidene
fluoride or dichlorodifluoroethylene.

As the raw material gas for use in the plasma
20 polymerization method, tetrafluoroethylene,
trifluoroethylene, vinyl fluoride, vinylidene fluoride
or dichlorofluoroethylene is used.

A fluororesin film having micropores can be used.

Composite Layer

25 The composite layer is selected from a group
consisting of the foregoing conductor, semiconductor and
insulating material. By using two or more types or raw

2
1 materials, the composite layer is formed by a sputtering
method of a CVD method. As an alternative to this, two
or more types of powder selected from a group consisting
of conductor powder, semiconductor powder and insulating
5 material powder are melted in a melted or dissolved
resin so that the film for use as the composite film is
manufactured.

Another structure may be employed as a preferred
structure in which the concentrations (content) of the
10 conductor, semiconductor and the insulating material in
the composite layer are change continuously or
discontinuously in the direction of the thickness of the
layer.

TELETYPE
X
15 The apertures in the layer can be formed in such a
manner that: an electrolyte is mixed with the raw
material at the time of applying the conductor,
semiconductor and the insulating material by the
sputtering method or the CVD method to add the
electrolyte into the conductor, semiconductor and the
20 insulating material. The foregoing electrolyte is
eluted into the electrolytic solution of the battery so
that a micropore structures are formed in the conductor,
semiconductor and the insulating material. Since
lithium ions and hydroxide ions can easily be introduced
25 and discharged in the micropores, the charging and
discharging efficiencies can be improved. Since the
pore has a small size, the growth of the dendrite can be

- 1 prevented, and therefore the life ^{of} ~~against~~ ^a the charging
and discharging cycle can be lengthened.

Stacked Structure

- 5 The conductor, semiconductor and the insulating
material layers may be formed into a single layer or a
multi-layer composed of two or more layers.

- The stacking method comprises a step of stacking a
film selected from the group consisting of the
conductor, semiconductor and the insulating material
10 between the negative pole and the separator. The film
is stacked on the surface of the negative pole, or
stacked between the negative pole and the separator in a
non-contact manner or stacked on the surface of the
separator. As an alternative to this, the negative pole
15 or the separator or a substance through which ions can
be passed may be used as the base on which the
conductor, semiconductor and the insulating material are
stacked by a sputtering method or a CVD method.

Thickness

- 20 The optimum thickness of the single, multi-layer or
the composite layer composed of the one or more types of
layers selected from the group consisting of the
conductor, semiconductor and the insulating material
differs depending upon the void ratio, the aperture
25 distribution, the material of the layers and the number
of layers. If the material includes a large volume gaps
as the polymer material, it is preferable the thickness

porosity

7/9/2

- 1 be 10 μm or thinner, more preferably 1 μm or thinner.
If a precise material such as the inorganic compound is used, it is preferable to make the thickness to be 1 μm or thinner, more preferably 1000 \AA or thinner.

5 Multi-Layer Metal Oxide

The multi-layer metal oxide 10102 must contain one or more types of materials selected from a group consisting of alumina, titanium oxide, silica, selenium oxide, zirconia oxide, magnesium oxide, chrome oxide, calcium oxide, tin oxide, indium oxide and germanium oxide.

The multi-layer metal oxide film is formed by molding a bimolecular film in a mold. By forming the metal oxide film by using the bimolecular film, a metal oxide film having small apertures and a large specific area and formed into a multi-layer film structure can be obtained.

Method of Preparing Multi-Layer Metal Oxide

The preparation is usually in such a manner that: a sol in which very fine particles of the metal oxide is, in a ~~colloid~~ ^{colloid} manner, dispersed in a solvent, such as water, is added to a ~~supersonic~~ ^{with ultrasonication} dispersion solution of water or buffer solution of a film forming compound for forming a bimolecular film selected depending upon the type of the sol and upon the surface charge so that a uniformly-dispersed solution is prepared; then it is developed on a fluororesin film or a glass plate

1 followed by developing the solution; and a cast film is
manufactured. If the uniformly-dispersed film cannot be
obtained, the^W any one of the following methods is
employed:

5 (1) A cast film is formed by adding a low-melting point
organic solvent, such as alcohol, chloroform, acetone or
tetrahydrofuran, is added to the film forming compound
and dispersing the materials, and then water or a buffer
10 solution is added to the solution from which the solvent
has been gradually evaporated, and then the mixture is
dispersed with ultrasonic waves.

(2) Water or a buffer solution is added to the cast
film described in (1), and the material is heated to a
level higher than the phase transition temperature of
15 the film.

(3) The film forming compound is dissolved in an
organic solvent, such as diethylether or ethylalcohol,
and the solution is injected into water and a buffer
solution.

20 As a method of obtaining the bimolecular film which
serves as the mold of the film shape of the metal oxide,
the mechanical strength can be improved by any one of
the following methods:

(a) The film forming compound is impregnated into a
25 porous polymer film to form the bimolecular solid film.

(b) A hydrophobic polymer or a hydrophilic polymer and
the film forming compound are dissolved in a solvent,

1 and the solution is developed so that a cast film is
obtained.

(c) A solution of a polymer electrolyte having a charge
opposing that of the ionic film forming compound is
5 mixed with a solution in which the ionic film forming
compound is dispersed so that sedimentation of polyion
complex is obtained, and then the polyion complex is
dissolved in an organic solvent followed by developing
it so that the cast film is obtained.

10 Alternatively, any one of the following methods
may be employed: a chloric acid (surface active agent)
method which is used at the time of preparing ribosome;
a freezing-melting method; an inverse-phase evaporation
method; and a macro-ribosome preparation method.

15 The film forming compound may be a compound having
both hydrophobic group and a hydrophilic group
(substance having amphipathic property) is used. The
film forming compound may be an ammonia compound, an
anion compound, a nonion compound and a polymerable
20 compound depending upon the molecular structure. The
hydrophobic group of the film forming compound is
categorized ~~to~~ a hydrocarbon, fluorine carbide,
unsaturated hydrocarbon, and unsaturated fluorine
carbide. A material containing a chromophore structure
25 introduced thereto in order to improve the molecular
orientation in the film forming compound may be used.

The film forming compound is exemplified by

- 1 p - octyloxyaniline hydrochloride,
 p - (octyloxy) - p' - hydroxyazobenzene,
 p - (10 - octyloxy) - p' - octyloxyazobenzene,
 dodecyl - N - [p - {p - (10 -
 y 5 bromodecyloxy)phenylazo}benzo[1]L - alaninate, L -
 glutamic acid didodecylester hydrochloride,
 N - [11 - bromoundecanoyl] - L glutamic acid
 didodecylester, dimethyldihexadecylammonium bromide, N -
 h/y 18 - (trimethylammonio)etyloxybenzo[1]didodecyl - L -
 10 glutamic acid bromide,
 dioctadecylmethyldimethylamm^oonium bromide, N - [11 -
 hydroxyundecanoyl] - L - glutamic acid
 ditetradecylester, N - [11 - phospho^oundecanoyl] - L -
 acid ditetradecylester, 1, 2 - bis
 15 (hexadecyloxycarbonyl) ethane - 1 - sulfonic acid
 sodium, N - [(2 - oxo - 1, 3, 2 - oxazaphosphoryl) - 11
 - oxadodecanoyl] - L - glutamic acid dido^oecylester, N -
 [(2 - trimethylammonio - ethylphosphonate)undecanoyl] -
 L - glutamic acid didodecylester, N - [(2 - amm^oonio -
 20 ethylphosphonate)undecanoyl] - L - glutamic acid
 didodecyl ester and 1, 3 - hexadecyl - 2 - polyethylene
 glycolylglyce^oline.

It is preferable that the surface of the multi-
 layer metal oxide film of a non-water-soluble battery of
 25 a type comprising the negative pole activating material
 which is lithium is subjected to lipophil^oic treatment
 using an organic metal compound such as a silane

- 1 coupling material or titanate coupling agent.

In order to lower the current density at the leading portion of the dendrite at the time of the charge and to prevent the growth of dendrite, the surface of the multi-layer metal oxide film on the negative pole side may be applied with a conductive material by evaporation or plating.

Very Fine Particle Sol of Metal Oxide

- The dispersed sol of very fine particles of the metal oxide is usually obtained by an acid, a base and water are added to an alcohol solution of an organic metal compound such as metal alkoxide as to be hydrolyzed to form colloid of the very fine particles of the metal oxide. The dispersion medium of the very fine particle sol is obtained by substituting ~~to~~ an organic solvent if necessary.

- The alkoxide is typified by tetramethoxysilane, tetraethoxysilane, aluminum isopropoxide, and titanium isopropoxide. Another metal organic compound such as acetyl acetone complex salt, alkyl metal compound, acetylacetone metal salt, naphthenate metal salt or octylate metal salt may be used.

- The very fine particles of the metal oxide can be obtained by another method for obtaining the same from the gas phase reaction of the vapor of the organic metal compound or the metal. The obtained very fine particles of the oxide are dispersed in a solvent so that a

1 dispersed sol is prepared.

If the negative pole activating material is lithium or lithium alloy, lithium ions relate to the battery reactions. In the case of an alkali battery comprising
5 the negative pole activating material which is zinc, hydroxyl ions relate to the same. The typical battery of a type comprising the negative pole activating material which is zinc is exemplified by a nickel-zinc battery and an air-zinc battery.

10 By covering the surface of the positive pole 104 of the battery with a film 12102 which is made of an insulating material or a semiconductor through which ions relating to the battery reactions can be passed,
A dendrite of lithium or zinc grown from the negative pole
15 101 through the separator 108 during the repetition of the charge and the discharge are not substantially brought into contact with the conductor or a collector in the positive pole 104. As a result, short circuits in the battery can be prevented, and therefore the life
20 of the secondary battery can be lengthened. Further, the safety can be improved.

Covering of Positive Pole of Secondary Battery

As the insulating material of the coating material of the positive pole of the secondary battery, any one
25 of the following materials may be used which is selected from a group consisting of a polymer of the derivative of a large ring compound, a polymer of the derivative of

- L
- 1 an aromatic hydrocarbon, fluoro-resin, silicon resin,
titanium resin, polyoxefin, inorganic oxide, nitride,
carbide and halide. It is effective for the positive
pole of the lithium secondary battery to be covered with
5 the polymer of the derivative of the large ring
compound, the polymer of the derivative of the aromatic
hydrocarbon or the fluoro-resin.

Polymer of Derivative of Large Ring Compound

- The large ring compound is a ring compound of a
10 type comprising hetero-atoms of one or more types
selected from a group consisting of oxygen, nitrogen,
sulfur and phosphorus. The large ring compound is a
ring polyether having hole each having a radius larger
than the radius of the lithium ion. The large ring
15 compound has one or more structures selected from a
group consisting of ring polyamine, ring polythioether,
azacrown ether, ring thioether, thiocrown ether,
cryptand, cyclam, nonactine, variomicine, thyracrown
which is a crown ether containing silicon atoms,
20 cyclodextrin, cyclofan, phthalocyanine and porphyrin
compound.
- K

The surface of the positive pole is covered with
the large ring compound by any one of the following
methods:

- 25 a. A polymer solution obtainable from
polymerization of the derivative of the foregoing large
ring compound is applied by a coating method such as

1 dipping, spraying, screen-printing or coating application method.

2 b. A mixture in which the derivative of the large
3 ring compound ~~is~~ mixed with the polymer serving as the
4 binder is applied and then crosslinked to form the film.

5 c. The derivative of the large ring compound is
6 used as a monomer to be dissolved in an electrolytic
7 solution, and then an electric field is applied to
8 electrolyze and polymerize the material so that the film
9 is formed on the surface of the positive pole.

10 d. The molded positive pole is immersed in a
11 solution of the derivative of the large ring compound,
12 which anion-polymerizes, so that the polymer film is
13 formed.

14 e. A polymer obtainable by heating and
15 condensing the large ring compound having an aromatic
16 ring and formaldehyde in a formic acid is applied.

17 f. The film is formed by sputtering of a polymer
18 of the large ring compound or the derivative of the
19 large ring compound or by plasma-polymerizing the large
20 ring compound.

21 An electrolyte may be mixed at the time of
22 forming the film. As a result, the wettability between
23 the electrolytic solution and the film can be improved,
24 causing ions to easily pass through the film.

25 The polymer for use~~s~~ as the coating solution may
be poly [(dibenzo - 18 - crown - 6) - co - formaldehyde]

1 or the like. The coating polymer can be newly formed
by the following polymerizing reactions: a large ring
compound having a carboxylic group or an amino group or
a hydroxyl group at the terminal group thereof is
5 condensed and polymerized so that polyamide is obtained
if the carboxylic group and the amino group react with
each other. If the carboxylic group and the hydroxyl
group react with each other, polyester can be obtained.
The vinyl compound of the large ring compound or diene
10 of the large ring compound can be obtained in the form
of an addition polymer by radical polymerization, cation
polymerization or anion polymerization. The starting
material in the radical polymerization may be
azobisisobutyronitrile (AIBN), benzoylperoxide (BPO) or t
15 - butylhydroperoxide. A starting material for the
cation polymerization is exemplified by an acid such as
 H_2SO_4 , H_3PO_4 , $HClO_4$, CCl_3CO_2H and Friedel-Craft
catalyzer such as BF_3 , $AlCl_3$, $TiCl_4$ or $SnCl_4$. A large
ring compound having an aromatic ring can be
20 polymerized by dehydrogenation in which the Friedel-
Craft catalyzer and an oxidizer are combined ~~to~~ each
other. A starting material for the anion polymerization
may be an alkaline metal compound or an organic metal
compound.

25 As the monomer of the large ring compound for
use in the polymerization may be crown ether/(+) - 18 -
crown - 6 - tetracarboxylic acid, 1, 5, 9, 13, 17,

RECEIVED
MILE
ST

with

- c 1 21 - hexathiacyclotetrasiloxan - 3, 11, 19 - triol, 1, 5, 9, 13 - tetrathiacyclohexadecan - 3, 11 - diol, 1 - aza - 12 - crown - 4, 1 - aza - 15 - crown - 5, 1 - aza - 18 - crown - 6, 1, 4, 10, 13 - tetra~~xy~~so - 7, 16 - only
- a 5 diazocyclooctadecan, 1, 4, 10 - trioxa - 7, 13 -
- e 6 diazacyclopentadecan, or 6, 8 - dioxabicyclo [3. 2. 1] - 7 - on. As an alternative to this, dibenzocrown ether can be used.
- 7/c / e

10 In the foregoing polymerization, a copolymer of two more types of derivatives of the large ring compounds or a copolymer of the large ring compound and another monomer may be used as well as the polymer of the derivatives of the large ring compounds. A polymer obtainable by introducing the derivative of the large

15 ring compound into a polymer by substitution may be employed.

When a battery is manufactured, a polymer must be selected so as not to be dissolved in the solvent of the electrolytic solution or the polymer crosslinking

20 reactions are caused to proceed so as not be dissolved in the electrolytic solution.

The derivative of the large ring compound having, at the terminative group thereof, carboxylic group or amino group or a hydroxyl group or having a

25 vinyl bond or a diene bond and a crosslinking material are mixed in the polymer serving as the binder, and then the mixed material is hardened. An accelerating

1 material may be mixed at this time. The crosslinking
material is selected from a group consisting of
i disocyanate, a polyisocyanate prepolymer, block
isocyanate, an organic peroxide, polyamine, oxime, a
5 nitroso compound, sulfur, a sulfur compound, selenide^m, a
magnesium oxide, a lead oxide and a zinc oxide. The
organic peroxide is exemplified by di - cumyl - peroxide,
2, 5 - dimethyl - 2, 5 - di - (t - butyl peroxy)
hexane, 1, 3 - bis - (t-butyl peroxy isopropyl)
10 benzene, 1, 1 - bis - (t-butyl peroxy) - 3, 3, 5 -
trimethyl - cyclohexane, n - butyl - 4, 4 - bis - (t -
butylperoxy) valerate, 2, 2 - bis - (t - butyl
peroxide) butane, t - butyl peroxy - benzene, and
vinyl - tris - (t - butyl peroxy) silane. As an
15 accelerating agent, a guanidine, aldehyde - amine,
aldehyde-ammonia, thiazol^e, sulfonamide, thiourea,
thiuram, dithiocarbamate, xanthate accelerating agent
is used.

Another coating method using the binder polymer
20 is exemplified by a method in which a mixture of the
large ring compound and the binder polymer is applied,
and then radial rays, electron rays or ultraviolet rays
are applied to cause the applied material to be
crosslinked.

25 As a method for covering the positive pole by
the electrolytic polymerization, a monomer, such as
dibenzocrown ether, is mixed in the electrolytic

1 solution, and then the electrolytic polymerization is
performed while using the negative pole activating
material or the conductive matrix as an anode. The
solvent of the electrolytic solution is exemplified by
5 acetone~~tr~~^{yl} (CH₃CN), benzonitr~~yl~~^{yl} (C₆H₅CN), propylene
carbonate (PC), dimethylformamide (DMF), tetrahydrofuran
(THF), nitrobenzene (C₆H₅NO₂), dichloroethane,
diethoxyethane, chlorobenzene, γ - butyrolactone, and
dioxolan~~y~~ and their mixtures.

10 It is preferable that the solvent be dehydrated
with active alumina, molecular ~~sieve~~, phosphorus
pentaoxide or calcium chloride.

The supporting electrolyte is an acid, such as
H₂SO₄, HCl or HNO₃ or salt composed of monovalent metal
15 ion (Li⁺, K⁺, Na⁺, Rb⁺ or Ag⁺) or tetraammonia ion
(tetrabutyl ammonia ion (TBA⁺) and tetraethyl ammonia
ion (TEA⁺)) and Lewis acid ion (BF₄⁻, PF₆⁻, AsF₆⁻ or
ClO₄⁻). It is preferable that the foregoing salt is
refined by re-crystallization or it is heated under
20 lowered pressure to sufficiently dehydrate and
deoxidize the salt.

As the monomer, crown ether/benzo - 15 - crown -
5, crown ether/benzo - 18 - crown - 6, crown ether/N -
phenylaza - 15 - crown - 5, crown ether/dibenzo - 18 -
25 crown - 6, crown ether/dibenzopyridino - 18 - crown - 6,
crown ether/dibenzo - 24 - crown - 8, 1, 13 - bis (8 -
quinolyl) - 1, 4, 7, 10, 13 - pentaioxatridecan, 5,

- 1 6 - benzo - 4, 7, 13, 16, 21, 24 - hexaoxa - 1, 10 -
C diazabicyclo [8. 8. 8] - hexa~~ox~~osan, 5, 6 - 14, 15 -
dibenzo - 4, 7, 13, 16, 21, 24 - hexaoxa - 1, 10 -
C diazabicyclo [8. 8. 8] - hexa~~ox~~osan, bis [(benzo - 15 -
y 5 crown - 5 -) - 15 - ~~1~~lmethyl] pimelate, crown
ether/dibenzo - 30 - crown - 10, N, N' - dibenzyl - 1,
A 4, 10, 13 - tetraoxa - 7, 16 - diazacycloox~~ad~~ecar., x
dilithiumphthalocyanin, 4' - nitrobenzo - 15 - crown -
5, 3, 6, 9, 14 - tetrathiabicyclo [9. 2. 1] tetradeca -
10 11, 13 - diene and their mixtures

Since the performance of the battery deteriorates if the polymer film for covering the surface of the negative pole activating material is dissolved in the electrolytic solution, it is preferable to be crosslinked.

It is preferable that the thickness of the film to be formed on the surface of lithium ranges from 10 \AA to 100 μ , further preferably ranges from 50 \AA to 10 μ . The optimum thickness of the film differs depending upon the density or the void ratio of the film and considerably differs depending upon the type of the electrolytic solution. The thickness of the film can be adjusted by changing the concentration of the main material in the coating liquid for forming the film.

25 Polymer of Derivative of Aromatic Hydrocarbon

As the derivative of the aromatic hydrocarbon for forming the charge moving complex is one or more

porosity

1 types of derivatives selected from a group consisting
of naphthalene, anthracene, phenanthrene, naphthacene,
pyrene, triphenylene, per~~ylene~~llene, picene, benzopyrene,
coronene and ovalene.

5 The polymer for use to form the coating
material can be prepared by polymerization or
copolymerization of vinyl monomer, monomer of
acetylene derivative or dicarboxylic acid and diamine,
and dicarboxylic acid and glycol. The polymerization
10 of the vinyl monomer can be performed by radical or
ion polymerization. The monomer of the acetylene
derivative can be polymerized while using a chloride
of tungsten as a catalyst. The dicarboxylic acid and
diamine can be polycondensed and the dicarboxylic acid
and glycol can as well as be polycondensed.^g well

15 The monomer of the aromatic derivative for
forming the polymer is exemplified by 2 - vinyl
naphthalene, 2 - vinyl pyridine, 9 - vinyl anthracene,
9, 10 - anthracene dipropionic acid, 9, 10 - bis
20 (phenyl ethyl) anthracene and 5, 12 - bis (phenyl
ethynyl) naphthalene.

A starting material for the radical
polymerization is exemplified by azobisisobutyronitrile
(AIBN), benzoylperoxide (BPO) and t - butylhydroperoxide.

25 A starting material for the cation polymerization is
exemplified by an acid such as H_2SO_4 , H_3PO_4 , $HClO_4$,
 CCl_3 or CO_2H and Friedel-Craft catalyst such as BF_3 ,

- 1 AlCl_3 , TiCl_4 or SnCl_4 . A large ring compound having an aromatic ring can be polymerized by dehydrogenation in which the Friedel-Craft catalyzer and an oxidizer are combined ~~to~~ each other. A starting material for the anion polymerization may be an alkaline metal compound or an organic metal compound.

- As an alternative to the foregoing method, a polymer into which an aromatic group can be obtained by subjecting the side chain of each polymer to a substitution reaction with a derivative of an aromatic compound. Another method may be employed in which an electrolytic polymerization reaction is caused to take place in an electrolytic solution containing a monomer mixed therein to form directly a polymer of an aromatic compound on the surface of positive pole.

- When the surface of the positive pole is applied with a coating by using the foregoing polymer solution, it is preferable to use a polymer solution dehydrated and deoxidized sufficiently in inactive gas dehydrated sufficiently. It is preferable to use a solvent in the foregoing solution which has been dehydrated with active alumina, molecular ~~sieve~~, phosphorus pentaoxide or calcium chloride. As an alternative to this, it is preferable depending upon the type of the solvent that the solvent be distilled ~~under~~ presence of alkaline metal in inactive gas to remove impurities and to be dehydrated.

1 An electrolyte may previously be mixed when the
foregoing film is formed. It leads to a fact that
wettability between the electrolytic solution and the
film can be improved, causing ions to easily pass
5 through the film.

 Since the performance of the battery deteriorates
if the polymer coating film is dissolved in an organic
solvent of the electrolyte, it is preferable to be
crosslinked in such a manner, for example, ultraviolet
10 rays, electron rays or radial rays are applied or a
crosslinking material, such as a radical generating
agent, is used.

Fluororesin

 The fluororesin for covering the surface of the
15 positive pole is exemplified by ethylene tetrafluoride-
ethylene copolymer, ethylene tetrafluoride chloride,
ethylene tetrafluoride - per - fluoroalkylvinyl ether
copolymer, ethylene tetrafluoride - propylene
hexafluoride copolymer, vinylidene fluoride resin,
20 vinyl fluoride resin, and ethylene tetrafluoride resin.
Since the foregoing materials are not dissolved in a
solvent, it is preferable to employ sputtering or
plasma polymerization to cover the surface of the
positive pole with the fluororesin.

25 Among the fluororesins, those having an ether
bond ~~is~~ able to facilitate the surface covering because
are they can easily be dissolved in a solvent and to improve

1 the affinity with lithium ions. The fluoro-resin having
the ether bond is exemplified by (6) a copolymer of ethylene
fluoride and vinyl monomer such as vinyl ether,
dioxysol, dioxyne or dioxycene having an ether bond or
5 dienemonomer derivative or a copolymer with a vinyl
monomer, such as vinyl ether, dioxysol or dioxyne,
dixycene having a fluorized ether bond with a diene
compound, such as ethylene. The fluoroethylene may be
a fluoroethylene derivative such as tetrafluoroethylene,
10 chlorotrifluoroethylene, vinylidene fluoride or vinyl
fluoride. The fluoroethylene copolymer containing the
ether bond can be polymerized by a solution, suspension,
block or emulsion polymerization. As a starting
material, a peroxide, alkyl boron, light or radial rays
15 may be employed.

The fluoro-resin can be coated on lithium metal
by any one of the following methods (7)

a. A solution of the fluoro-resin is applied by
spraying, screen printing, by using a coater or by
20 dipping.

b. The fluoro-resin is directly coated to the
surface of ~~lithium~~ by a vacuum evaporation method such
as sputtering.

c. A polymer film is directly formed by plasma
25 polymerization under an atmosphere of monomer which is
the raw material for the fluoro-resin.

If the lithium surface is coated by using the

THESE

positive pole

the surface of the positive pole

③

②

1 fluororesin solution, it is preferable to use, in an
inactive gas dehydrated sufficiently, a fluororesin
solution dehydrated and deoxidized sufficiently. It is
preferable to use a solvent in the foregoing solution
5 which has been dehydrated with active alumina, molecular
ie ~~sheave~~, phosphorus pentaoxide or calcium chloride. As
an alternative to this, it is preferable depending upon
the type of the solvent that the solvent be distilled
under presence of alkaline metal in inactive gas to
10 remove impurities and to be dehydrated.

TECHNICAL
15 An electrolyte may previously be mixed when the
foregoing film is formed. It leads to a fact that
wettability between the electrolytic solution and the
film can be improved, causing ions to easily pass
through the film.

Since the performance of the battery deteriorates
if the fluororesin film is dissolved in an organic
solvent of the electrolytic solution, it is preferable
that the film is crosslinked.

20 As an alternative to the foregoing method of
coating the surface with the fluororesin solution having
the ether bond, another method may be employed in which
ethylene fluoride and vinyl monomer are used as the main
so raw material ~~as~~ to be plasma-polymerized so that the
25 surface is covered. In order to ~~easily~~ cause the plasma *α*
polymerization to take place easily or to improve the
contact of the film and the strength of the same, it is

- 1 preferable to add, to the fluorine compound serving as
the raw material, oxygen, hydrogen, helium, argon,
nitrogen, silane, hydrocarbon or the like. The plasma
can effectively be generated by a DC or RF glow
5 discharge method, a microwave discharge method or a
laser beam irradiation method. The fluororesin having
the ether bond may be sputtered to cover the surface of
the positive pole.

It is preferable that the thickness of the film
10 to be formed on the surface of lithium ranges from 10 \AA
to 100 \mu , more preferably ranges from 50 \AA to 10 \mu .
The optimum thickness of the film differs depending
upon the density or the void ratio of the film and
considerably differs depending upon the type of the
15 electrolytic solution. The thickness of the film can
be adjusted by changing the concentration of the main
material in the coating liquid for forming the film.
If the plasma polymerization or sputtering is performed,
the thickness can be adjusted by controlling the
20 deposition time period.

Silicon Resin

The organic silicon compound may be any one of
a material selected from a group consisting of
alkoxysilane, alkylsilane, halogenated silane, siloxane,
25 silane containing vinyl group, amino group, epoxy group,
methacrylic group or mercaptan group introduced thereto,
hydrogen - denatured, vinyl - denatured, hydroxyl group

- 2
- 1 denatured, amino - denatured, carboxylic group
denatured, chloro - denatured, epoxy denatured,
methacryloxy - denatured, mercapto - denatured,
fluorine - denatured, long-chain-alkyl denatured or
5 phenyl - denatured polysiloxane, alkylene oxide
denatured siloxane copolymer, silicon - denatured
copolymer, alkoxysilane - denatured polymer, silicon -
denatured urethane or silicon - denatured nylon.

10 If the organic compound is liquid, the film can
be formed by a direct coating method or the organic
compound is diluted in a solvent and then applied. If
the organic compound is solid, a solution dissolved in a
solvent may be applied. The application method may be a
dipping method, a screen printing method, a spraying
15 method, a roll coating method or the like. The
viscosity of the coating solution must adequately be
adjusted to be adaptable to the coating method.

FOR RELEASE
1964
104

Titanium Polymer

20 A titanium polymer obtained by causing an
organic titanium compound to act on an organic polymer
may be used. For example, a thiranopolymer of silicon
polymer formed by crosslinking the main chain of a
polycarbosilane skeleton with the titanium organic
compound may be used.

25 As an alternative to the titanium polymer, a
material obtained by introducing the derivative of an
organic metal compound, such as an organic aluminum

1 compound, into a polymer by substitution reactions may
be used as the coating material.

Polyphosphazene

5 Polyphosphazene which is a polymer in which
phosphor atoms and nitrogen atoms alternately form
phosphor-nitrogen double bonds can be obtained by
heating a dichloropolyphosphazene trimer to 200 to
300°C and by ring-opening polymerization. The
dichloropolyphosphazene trimer can be synthesized from
10 phosphorus pentachloride and ammonia chloride or
ammonia. Any one of the following cataly~~zer~~ is used at
the time of the polymerization: benzoic acid, sodium
benzonate, 2, 6 - di - p - cresol, water, methanol,
ethanol, nitromethane, ether, heteropoly acid, sulfur,
15 zinc, tin and sodium.

Further, various type~~y~~ of polyorganophosphazene
can be obtained by substituting chloride atoms of
polydichlorophosphazene by an organic reagent or an
organic metal reagent.

20 If the surface of positive pole is coated with
the foregoing polyphosphazene, it is preferable that the
polymer solution dehydrated and deoxidized sufficiently
be used in inactive gas dehydrated sufficiently. It is
preferable to use a solvent in the foregoing solution
25 which has been dehydrated with active alumina, molecular
sie~~ve~~, phosphorus pentaoxide or calcium chloride. As
an alternative to this, it is preferable depending upon

TEE TEE TEE TEE TEE TEE TEE TEE TEE TEE

sts

s

ie

1 the type of the solvent that the solvent be distilled
in the ~~under~~ presence of alkaline metal in inactive gas to
remove impurities and to be dehydrated.

An electrolyte may previously be mixed when the
5 foregoing film is formed. It leads to a fact that
wettability between the electrolytic solution and the
film can be improved, causing ions to easily pass
through the film.

Since the performance of the battery deteriorates
10 if the polymer coating film is dissolved in an organic
solvent of the electrolyte, it is preferable to be
crosslinked in such a manner, for example, ultraviolet
rays, electron rays or radial rays are applied or a
crosslinking material, such as a radical generating
15 agent, is used.

It is preferable that the thickness of the film
to be formed on the surface of lithium ranges from 10 \AA
to 100μ , more preferably ranges from 50 \AA to 10μ .
The optimum thickness of the film differs depending upon
20 the density or the void ratio of the film and
considerably differs depending upon the type of the
electrolytic solution. The thickness of the film can
be adjusted by changing the concentration of the main
material in the coating liquid for forming the film.

25 Polyolefin

As polyolefin, polyethylene or polypropylene may
be used. Polyolefin is used in such a manner that the

- 1 positive pole is dipped in a solution dissolved in a
solvent such as tetrahydrofuran or o-dichlorobenzene,
the positive pole is then dried and crosslinked by
ultraviolet, electrons, radial rays or the like so that
5 the film is formed on the surface of the positive pole.

The film can be formed by sputtering or plasma
CVD method. In the material in the plasma CVD method,
ethylene gas or propylene gas may be used.

Inorganic Oxide

- 10 The inorganic glass is made of a material, such
as silica, titanium oxide, alumina, zirconia oxide,
magnesium oxide, tantalum oxide, molybdenum oxide,
tungsten molybdenum, tin oxide, indium oxide, iron
oxide, chrome oxide, aluminum phosphate, iron phosphate,
15 silicon phosphate and their mixtures. A sol-gel method
is one of adequate methods for forming the inorganic
glass. The raw material for the material having the
inorganic glass structure is obtained in such a manner
that an acid or a base and water are added to a solution
20 of alcohol of an organic metal compound such as a metal
alkoxide to hydrolyze the raw material so as to form
colloid particles having metal atom-oxygen atom bonds,
and then the colloid solution is directly applied to the
surface of the positive pole. As an alternative to
25 this, a solution in which a monomer or an organic
polymer or the organic polymer and a crosslinking
material are dissolved in the colloid solution is

o/al

o/al

1 applied, and then the solution is polymerized or dried
and polymerized so that the film is formed. By forming
the composite organic polymer, strength against cracks
and separation can be improved. If the electrolyte
5 forming the lithium battery is dissolved in the collid~~e~~ o/al
solution to form the film, the wettability with the
electrolytic solution can be improved and ions are
enabled to move easily. /

As an alternative to alkoxide, any one of the
10 following organic metal compound may be employed: A
acetyl acetone complex salt, an alkyl metal compound,
acetyl acetone metal salt, naphthene acid metal salt,
and octyl acid metal salt.

The organic polymer for combining the organic
15 polymers is exemplified by epoxy resin, polyester,
polyimide, polyethylene, polypropylene, polyurethane,
polystyrene, polyethylene glycol, nylon, fluorine resin
and silicon resin.

The polymer crosslinking material is exemplified
20 by diisocyanate, polyisocyanate prepolymer, block
isocyanate, organic peroxide, polyamine, oxims, nitroso e
compound, sulfur or sulfur compound, selenium, magnesium
oxide, lead oxide and zinc oxide.

As an alternative to using the crosslinking
25 material, a method may be employed in which radial rays
or electron rays or ultraviolet rays are applied to
polymerize or crosslink the polymer.

1 As an application method, a dipping method, screen
printing, spraying or a roll coating method may be
employed. The viscosity of the liquid to be applied
must adequately be adjusted to be adaptable to the
5 application method.

Another method of forming the film by the glass
inorganic oxide may be employed for example, any one of
the following evaporation method or a CVD method may be
employed: a sputtering method, an electron beam
10 evaporation method, a plasma CVD (Chemical Vapor
Deposition) method, and a laser CVD method.

The sputtering process and the electron beam
evaporation can be performed by a method in which the
oxide material is directly evaporated or by a method in
15 which silicon or metal vapor and oxygen gas are caused
to react with each other to form the film.

The plasma CVD method and the laser CVD method is
performed in such a manner that oxygen gas and any one
of a hydroxide or halide of silicon or metal and an
20 organic metal compound are used as the raw materials to
be decomposed by discharge or laser so that the film is
formed.

The inorganic oxide can be used to form the film
by another method, that is, an electrochemical method
25 comprising the steps of forming a metal film made of
aluminum, titanium, tantalum, niobium by sputtering or
electron beam, anode-oxidizing the film by using an

1 oxalic acid, a phosphoric acid or ammonia borate as an electrolytic solution to form the oxide film.

- /
5 A film forming method may be employed which utilizes the equilibrium reaction in the water solution to precipitate and cause the oxide film to grow on the surface of the dipped substrate. In this case, silica (a silicon oxide), titanium oxide or vanadium oxide film can be formed. A specific method of forming the silica film comprises the step of dipping the positive pole in
10 a solution in which silica is saturated in a water solution of hydrofluosilicic acid to form the film.

Nitride

15 The nitride can be obtained from silicon nitride, titanium nitride, aluminum nitride or boron nitride or the like. The nitride film can be formed on the positive pole by sputtering, an electron beam evaporation method, a plasma CVD method or a laser CVD method.

20 The sputtering and the electron beam evaporation methods are categorized to a method in which the nitride material is directly evaporated and a method in which vapor of silicon, titanium or aluminum and nitrogen plasma generated from nitrogen gas or ammonia gas are caused to react with each other to form the film.

25 The plasma CVD method and the laser CVD method respectively comprise the step of decomposing the raw material gas, such as nitrogen gas, ammonia gas or

1 nitrogen trifluoride and a hydroxide such as silicon,
titanium or aluminum, halide or an organic metal
compound by discharge or laser to form the film.

Carbide

5 The carbide can be obtained from a material
exemplified by amorphous carbon, silicon carbide,
titanium carbide, vanadium carbide and tungsten carbide.

The carbide film can be formed by a similar
method employed to form the nitride.

10 The sputtering and the electron beam evaporation
methods are categorized to a method in which the
material from which the carbide is obtained is directly
evaporated and a method in which silicon, titanium,
vanadium or tungsten and carbon are used as the raw
15 materials to form the film.

The plasma CVD method and the laser CVD method
respectively comprise the step of, by laser, decomposing
the material, such as hydrocarbon, from which carbon is
obtained and a hydroxide such as silicon, titanium,
20 vanadium or tungsten or a halide or an organic metal
compound to form the film.

Halide

The halide can be obtained from a material
selected from a group consisting of lithium fluoride,
25 magnesium fluoride, sodium fluoride, potassium fluoride,
barium fluoride or lithium chloride.

The halide film can be formed by a sputtering

1 method or an electron beam evaporation method. A CVD
method such as the plasma CVD method or the laser CVD
method may be employed.

Semiconductor

5 The semiconductor for covering the positive pole
is made of a material exemplified by diamond (carbon),
silicon, nickel oxide, copper oxide, vanadium oxide, tin
oxide and zinc oxide.

Alkali metal, phosphorus or boron may be added
10 as impurities.

The semiconductor film may be formed by
sputtering, electron beam evaporation, plasma CVD or
laser CVD as well as the foregoing method of forming
the inorganic acid film.

15 Covering of Positive Pole of Nickel-Zinc Secondary
Battery or Air-Zinc Secondary Battery

The material and the method of covering the
positive pole of a nickel-zinc secondary battery or air-
zinc secondary battery may be the same as those employed
20 to cover the positive pole of the lithium secondary
battery. Also, a polymer of a type which is dissolved in
an organic solvent but which is not dissolved in water
may be used. If the covering material has water,
repellant characteristics, a hydrophilic group must be
25 introduced or must be subjected to hydrophilic treatment
using a silane coupling material.

1 Thickness of Film Covering the Surface of Positive Pole

The thickness of the film for covering the surface of the positive pole can be controlled by adjusting the concentration of the solution if the surface is covered by utilizing the liquid layer reactions performed by the polymer solution or the sol-gel method. The same can be controlled by adjusting the deposition time if sputtering, the electron beam evaporation, the CVD method or the plasma polymerization is employed.

10 Aperture, in Coating Film on Positive Pole Surface

The apertures and the void ratio of the coating film for covering the surface of the positive pole can be controlled by adjusting the concentration of the solution or the drying condition if covering is performed by using the polymer solution or by utilizing the sol-gel method. Further, any one of the following methods may be employed: a method for forming the film while causing foam to be generated by adjusting the concentration of the foaming material; a method having the steps of forming a film in which the content of the electrolyte is adjusted, and dissolving the electrolyte; a method for controlling the evaporation rate; and a method for adjusting the mixture ratio of the reactive materials.

25 If the negative pole is covered with the coating material of a type employed to cover the positive pole, growth of dendrite, from the negative pole can be

A
positivity

A

7 prevented. Therefore, short circuits in the battery can be prevented ^{by} ~~an effect obtainable from~~² covering the positive pole. As a result, the battery cycle can further be lengthened.

5 Then, a positive pole according to the present invention composed of transition metal and group ~~6~~A element will now be described.

Transition Metal Element

The transition metal element in the positive pole activating material according to the present invention may be an element having partially shell d or shell f and selected from a group consisting of T, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Wn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au. Any one of the first transition system metal¹ is mainly used which is exemplified by Ti, V, Cr, Mn, Fe, Co, Ni or Cu. A compound of the transition metal and the group ~~6~~A element is manufactured by a material exemplified by the transition metal, the salt of the transition metal, an oxide of the transition metal and a hydroxide of the transition metal.

Group ~~6~~A Element

The positive pole activating material according to the present invention comprises the group ~~6~~A element exemplified by O, S, Se, Te and Po. Among the foregoing elements, O or S is mainly employed. A compound of the transition metal and the group ~~6~~A element can be

1 manufactured by a material exemplified by a compound of
a hydroxide, halide, halide oxide or oxide of sulfur,
ium selen~~o~~, tellurium, polonium.

Additive Element

5 By adding elements except the transition metal,
the distortion of the positive pole activating material
occurring due to the introduction/discharge of lithium
ions can be relaxed. The element can be effectively
added by a method comprising the step of adding the
10 salt, the halide or an organic metal compound of one or
more types of elements selected from a group consisting
of lithium, magnesium, sodium, potassium, aluminum,
zinc, calcium, barium, lead, indium, boron, silicon,
tin, phosphor~~y~~, arsenic, antimony, bismuth, chlorine and
15 fluorine. It is preferable that the atom ratio of the
additive element with respect to the transition metal
element be 1 or less.

Method of Manufacturing Compound of Transition Metal and
Group ~~IA~~ Element

20 The compound of the transition metal and the
group ~~IA~~ element according to the present invention is
manufactured by any one of ^{the following} ~~methods~~ ~~categorized~~ to a
method in which the compound is prepared from the
solution of the salt of the transition metal or the
25 organic transition metal compound by way of a hydroxide,
a method comprising the steps of melting the transition
metal or the transition metal compound and rapidly

The method of preparing the transition metal oxide from the hydroxide is exemplified by a method comprising the step of baking or drying hydroxide in air or in an oxygen atmosphere to prepare powder. A specific example of preparing the transition sulfide from the hydroxide is exemplified by a method comprising the step of baking a hydroxide in a hydrogen reduction atmosphere in which a hydrogen sulfide is mixed to prepare powder.

The rapid cooling method for preparing the transition metal oxide comprises the steps of melting the transition metal compound, such as the transition metal or the transition metal oxide, and spraying oxygen gas containing inactive gas mixed thereto to a rotating disc to prepare the powder.

The method of preparing the transition metal oxide by the gas phase reactions comprises the step of oxidizing or hydrolyzing the salt of the transition metal or causing vapor of the transition metal to react with the group 6A element or a compound of the group 6A element or decomposing the organic transition metal compound to prepare the powder.

25 It is preferable that each process be performed
at 400°C or lower, more preferable 300°C or lower.

The liquid phase reaction method, the gas phase

1 reaction method and the melting and rapid cooling method
will now be described.

Liquid Phase Reaction

A method of preparing the hydroxide for use in
5 the main reaction in the method of manufacturing the
material from the solution by way of the hydroxide is
exemplified by:

Method of Preparing Hydroxide

It is preferable that the transition metal
10 hydroxide be prepared by reactions between the salt of
the transition metal and alkali or by hydrolysis of the
organic transition metal compound or by reactions
between the transition metal and alkali. It is
preferable that the preparation temperature be 150°C
15 or lower, more preferably 100°C or lower.

Reactions between Salt of Transition Metal and Alkali

By causing alkali to react with the salt of the transition metal, a hydroxide of the transition metal is sedimentated to be prepared. By mixing salts of two or more types of the transition metals, a hydroxide of a composite transition metal can be obtained.

The salt of the transition metal is typified by a carbonate, a nitrate, a halide, a sulfate, a sulfamate, acetate, oxalate, citrate, tartrate, formate or ammonate.

The alkali may be lithium hydroxide, sodium hydroxide, potassium hydroxide or ammonia hydroxide. As

1 an alternative to this, urea or thiourea may be used
which raises the pH by generating hydroxide ions when
heated.

5 It is preferable that an organic acid or
inorganic acid or an amine is, in a small quantity,
added or an organic solvent such as alcohol is added
at the time of causing alkali to react with the water
solution of the transition metal salt in order to ^{make} fine
the sediment particles of the hydroxide. (7)

10 By vibrating the sediment with ultrasonic waves,
the sediment particles can be ^{made fine} ~~finer~~. Therefore, the
specific area can be enlarged. (7)

Hydrolysis Reaction of Organic Transition Metal Compound

15 The hydroxide of the transition metal can be
prepared by hydrolyzing an organic metal compound of the
transition metal, such as alkoxide, acetyl acetate,
octylate or naphthalate. 0

20 The hydrolysis of alkoxide is specifically
performed in such a manner that alkoxide of the
transition metal is dissolved by water, alcohol or
ethanol amine or the like, and an inorganic acid such as
hydrochloric acid or an organic acid such as acetic acid
or ammonia hydroxide or amine is added.

25 The alkoxide of the transition metal may be a
material selected from a group consisting of
 $Mn(OC_2H_5)_2$, $Mn(OC_3H_7)_2$, $Mn(OC_4H_9)_2$, $Ni(OC_2H_5)_2$, $Ni(OC_3H_7)_2$,
 $Ni(OC_4H_9)_2$, $Co(OC_2H_5)_2$, $Co(OC_3H_7)_2$, $Co(OC_4H_9)_2$.

008707.054
FEB 20 1960

1 $\text{Ti}(\text{OC}_2\text{H}_5)_2$, $\text{Ti}(\text{OC}_3\text{H}_7)_2$, $\text{Ti}(\text{OC}_4\text{H}_9)_2$, $\text{Fe}(\text{OC}_2\text{H}_5)_2$,
 $\text{Fe}(\text{OC}_3\text{H}_7)_2$, $\text{Fe}(\text{OC}_4\text{H}_9)_2$, $\text{Cu}(\text{OC}_2\text{H}_5)_2$, $\text{Cu}(\text{OC}_3\text{H}_7)_2$,
 $\text{Cu}(\text{OC}_4\text{H}_9)_2$, $\text{VO}(\text{OCH}_3)_3$, $\text{VO}(\text{OC}_2\text{H}_5)_3$, $\text{VO}(\text{OC}_3\text{H}_7)_3$,
 $\text{VO}(\text{OC}_4\text{H}_9)_3$ and $\text{Y}(\text{OC}_4\text{H}_9)_3$.

5 The acetylacetonate of the transition metal is
exemplified by $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2$,
 $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{H}_2\text{O})_2$, $\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{H}_2\text{O})_2$,
 $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{Ti}(\text{OC}_4\text{H}_9)_2(\text{C}_5\text{H}_7\text{O})_2$,
 $\text{La}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{Y}(\text{C}_5\text{H}_7\text{O}_2)_3$, and $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$.

10 The octylate of the transition metal is
exemplified by $\text{Cu}(\text{C}_7\text{H}_{15}\text{COO})_2$, $\text{Ni}(\text{C}_7\text{H}_{15}\text{COO})_2$, $\text{Fe}(\text{C}_7\text{H}_{15}\text{COO})_2$,
 $\text{Mn}(\text{C}_7\text{H}_{15}\text{COO})_2$, $\text{Co}(\text{C}_7\text{H}_{15}\text{COO})_2$, $\text{Zr}(\text{C}_7\text{H}_{15}\text{COO})_2$, $\text{Y}(\text{C}_7\text{H}_{15}\text{COO})_2$,
and $\text{La}(\text{C}_7\text{H}_{15}\text{COO})_2$.

hal
15 The naphthate of the transition metal is
exemplified by the salt of naphthate expressed by a
general formula $\text{C}_n\text{H}_{2n-2}\text{O}_2$, that is, cobalt naphthenate,
copper naphthenate, manganese naphthenate, iron
naphthenate, nickel naphthenate, vanadium naphthenate,
yttrium naphthenate and lanthanum naphthenate.

20 The alcohol is exemplified by methyl alcohol,
ethyl alcohol, isopropyl alcohol, ethylene glycol and
propylene glycol.

Dehydrating Reaction

25 In order to obtain the oxide of the transition
metal by dehydration from the transition metal hydroxide
prepared by the foregoing solution reactions, it is
preferable that the transition metal hydroxide is

1 immersed in an organic solvent such as alcohol or
acetone which is mixed with water to sufficiently
substitute water, and then it is dried in a vacuum state
at 100°C or higher. As an alternative to this, heating
5 and dehydration is performed by using microwaves. If
the drying temperature is too high, crystallization is
enhanced and therefore the hydroxide groups are
decreased. Therefore, it is preferable that the
temperature be 400°C or lower. It is preferable that
10 the frequency of the microwaves be a frequency which
can easily be absorbed by water.

In order to enlarge the specific area, another
method may be employed in which the dehydration is
performed by freezing and drying.

15 Hydrogen Treatment

Hydrogen is mixed into the dried atmosphere at
the time of drying the transition metal oxide followed by
performing heat treatment. As an alternative to this, a
method is employed in which the transition metal
20 hydroxide or the transition metal oxide is subjected to
hydrogen plasma treatment. The hydrogen plasma can be
generated by a hydrogen gas discharge method or by a
method of exciting and decomposing the hydrogen gas by
laser beams.

25 Introduction of Group 6A Element Except Oxygen

A method is employed in which the transition
metal hydroxide or the transition metal oxide is treated

VI
1 with hydrogen sulfide or hydrogen selenide or the group
IIA element is mixed at the time of preparing the
transition metal hydroxide.

Gas Phase Reaction Method

5 As a method of preparing a compound of the
transition metal and the group IIA element, a gasified
transition metal salt or an organic transition metal
compound or vapor of the transition metal and the group
VI / VI
IIA element or the group IIA element compound are caused
10 to react with each other in the gas phase to prepare
powder. Another method may be employed in which the
gasified transition metal salt or the organic transition
metal compound containing the group IIA element is
decomposed in the gas phase to prepare the compound of
15 the transition metal and the group IIA element.

AD
20 If the transition metal salt or the organic
transition metal compound is in the form of solid, it is
heated as to be formed into vapor or it is heated as to
be formed into liquid. Then, carrier gas is bubbled as
to be introduced into the reaction chamber. If the
transition metal salt or the organic transition metal
compound is in the form of liquid, it may be heated as
to be formed into vapor or carrier gas is bubbled as to
be introduced into the reaction chamber.

25 The salt of the transition metal may mainly be a
halide such as a chloride. As an alternative to this, a
carbonate, a nitrate, a sulfate, sulfonate, acetate,

1 citrate, tartrate, formate or ammonate. The chloride is exemplified by VOCl_3 , MnCl_2 , MoCl_5 , TiCl_4 , NiCl_2 , CoCl_2 , FeCl_3 , WCl_6 , YCl_3 and ZrCl_4 .

The raw material from which the group βA element
5 can be obtained is exemplified by the group βA element,
the hydroxide of the group βA element and the halide of
the group βA element.

By mixing hydrogen gas in the foregoing gas phase reaction, a compound of the transition metal and the group 6A element containing hydrogen can be prepared.

In the foregoing gas phase reaction, it is preferable to employ any one of the following methods: a heat CVD (Chemical Vapor Deposition) method, a plasma CVD method, a laser CVD method, a filament method, a reactive sputtering method and the electron beam method.

1) Sputtering is performed by heat in the heat CVD method, by ~~charge~~ in the plasma CVD method, by heat energy or light energy of laser beams in the laser CVD method, by heat of a filament made of tungsten or the like in the filament method, and in the reactive sputtering method in the reactive gas atmosphere, and by electron beam heating in the electron beam method. As a result, gas phase reactions are respectively performed so that the material is prepared. It is preferable that the raw material be in the form of a solid in the reactive sputtering method or the electron beam method.

1 Rapid Cooling Method

AD

In this case, any one of the following methods may be employed: a gun method comprising the steps of generating, while breaking a Mylar film, shock waves by helium gas, in which oxygen or hydrogen sulfide is mixed, as to be sprayed to the transition metal or the transition metal compound melted with high frequency waves, and causing blown compound powder to impact against a cooling steel plate in the form of a slide disposed below so that the temperature is rapidly cooled; a method in which a molten bath is dispersed by spraying with inactive gas jet in which oxygen or hydrogen sulfide is mixed; and an atomization method in which molten bath of the transition metal or the transition metal compound is sprayed in an atmosphere containing the group βA element such as oxygen or group βA element compound such as hydrogen sulfide as to be formed into powder. By mixing hydrogen gas into the inactive gas, hydrogen can be introduced into the product.

10

15

20

y

It is preferable that the rapid cooling rate be 10^1 to 10^8 K, more preferably 10^2 to 10^8 K.

The melting and heating furnace may be a crucible furnace, an induction furnace, an arc furnace or an electron beam furnace.

25

The method of causing the alkali to directly react with the transition metal is exemplified by a

- 1 method in which metal such as vanadium is caused to react
with molten alkali to prepare an oxide.

Conductor Core

- 5 When conductor powder is mixed at the time of
preparing the compound of the transition metal and the
group β A element to cause the compound of the transition
metal and the group β A element to grow while using the
conductor powder as the core, the collecting efficiency
can be raised. Therefore, the introduction and
10 discharge of lithium ions can be made easier, and
therefore the battery capacity can be enlarged.

- The conductor powder may be made of one or more
types of materials selected from a group consisting of
carbon, titanium, nickel, cobalt, iron, chrome,
15 manganese, vanadium, platinum, ~~par~~adium, copper, silver,
gold, zinc, tin, indium, lead, tungsten and molybdenum. *ll*
It is preferable to use one or more types of elements
selected from a group consisting of carbon, titanium,
nickel, cobalt, iron, chrome, manganese, vanadium and
20 platinum.

- The shape of the conductor powder is formed into
one or more types of shapes selected from a group
consisting of a spherical shape, a flake shape, a needle
shape and a fiber shape. As a result, also the compound
25 powder of the transition metal and the group β A element
can be formed into the spherical, flake, needle or fiber
shape. Therefore, the efficiency of the electron *VI*

1 movement between the positive pole activating material
can be raised, and therefore the charging and
discharging efficiency can be improved.

It is preferable that the diameter of the
5 conductor powder be 10 \AA to 100μ when measured by an
electron microscope, more preferably 10 \AA to 10μ .

Crushing of Positive Pole Activating Material

AD
The prepared positive pole activating material
must be crushed, as to have an adequate grain size if
10 obtained positive pole activating material is in the
form of a block.

It is preferable to crush the positive pole
activating material by using, while combining, means
selected from a group consisting of a compression
15 crushing machine, a shearing crushing machine, an impact
crushing machine, a roll mill, a roller mill, a high-
speed rotational mill, a ball mill, a medium stirring
mill, a jet mill, a mortar and a stamping mill.

Coating Film Made of Conductor

20 The prepared compound of the transition metal and
the group VA element is covered with a conductor thin
film by chemical plating (~~non-electrolytic~~ ^{electroless} plating) or
by evaporation. As a result of the foregoing process,
the current collecting efficiency can be raised, the
25 ~~introduction/discharge~~ ^{intercalation/deintercalation} of lithium ion can be
facilitated and the battery capacity can be enlarged.

The conductor thin film may be made of one or

1 more types of materials selected from a group
consisting of carbon, titanium, nickel, cobalt, iron,
chrome, manganese, vanadium, platinum, ~~pa~~adium, copper, *ll*
silver, gold, zinc, tin, indium, lead, tungsten and
5 molybdenum. It is preferable to use one or more types
of elements selected from a group consisting of carbon,
titanium, nickel, cobalt, iron, chrome, manganese,
vanadium and platinum.

The chemical plating method is a method in which
10 metal ions are deoxidized by a deoxidizer such as
formaldehyde to precipitate the metal film.

The evaporation is performed by any one of the
following methods: a method in which vapor of metal is
generated by electron beams or laser beams, *as to be* *so*
15 applied to the subject; a method in which a carbon or
metal target is sputtered, *as to be applied to the* *so*
subject; a method in which hydrocarbon or organic
solvent or an organic metal compound is decomposed by
discharge or laser or heat, *as to be applied to the* *so*
20 subject. The decomposition of the hydrocarbon and the
organic solvent enables a carbon film to be formed,
while the decomposition of the organic metal compound
enables a metal film to be formed.

It is preferable that the thickness of the
25 conductor film ranges from 50 \AA to 1 μ .

Lipophilic Treatment

The positive pole activating material is

1 subjected to the lipophilic treatment in such a manner
that the organic metal compound is immersed in a
solution, in which an organic solvent is dissolved,
and then it is dried.

5 It is preferable that the organic metal compound
for use in the lipophilic treatment be an organic metal
compound such as silane coupling material or organic
titanate. If dilution is performed, the dilution
concentration with respect to the solvent ranges from
10 0.05 to 2 wt%.

COPIED
FROM
0
0
d
The silane coupling material is exemplified by
vinyltrimethoxysilane, vinylmethoxysilane, N - (2 -
aminoethyl)-3 - aminopropylmethyl dimethoxysilane, N -
(2 - aminoethyl)-3 - aminopropyltrimethoxysilane,
15 3 - aminopropyltriethoxysilane, 3 -
glycidxypropyltrimethoxysilane, 3 -
glycidxypropylmethyldimethoxysilane, 2 - (3,4 -
epoxycyclohexyl) ethyltrimethoxysilane, 3 -
chloropropylmethyldimethoxysilane, 3 -
20 chloropropyltrimethoxysilane, 3 -
methacryloxytrimethoxysilane, 3 -
mercaptotrimethoxysilane, and N - [2 -
b/y (vinylbenzylamino)ethyl] - 3 -
aminopropyltrimethoxysilane.

25 The organic titanate is exemplified by tetra -
i - propoxytitanium, tetra - n - butoxytitanium, tetrakis
(2 - ethylhexyloxy)titanium, tetrastearoxytitanium,

1 di - i - proxy.bis (acetylacetate)titanium,
 dihydroxy.bis (lactato)titanium, titanium - i -
 propoxyoctylene glycol, titanium stearate, propane
 dioxytitanbis (ethylacetoacetatē), propanedioxytitanium
 5 (acetylacetonate) (ethylacetoacetate), oxotitanbis
 (monoammonium oxalate), tri - n -
 butoxytitanmonostearate, and titan polymer.

Analysis of Transition Metal and Group A Element

Measurement of Size of Crystal Grain

10 The size of crystal grains was evaluated from
 the peak half width and the angle of diffraction of
 X-ray diffraction curve in accordance with the following
 Scherrer's Formula:

$$t = 0.9\lambda / B \cos \theta_B \quad (\text{Scherrer's Formula})$$

15 where t: size of crystal grain

λ : wave length of X-ray beam

B: peak half width

θ_B : angle of diffraction

20 It is preferable that the average size of the
 crystal grain of the positive pole activating material
 which is the compound of the transition metal and the
 group A element for use in the secondary battery
 according to the present invention be 500 Å or less when
 calculated by using the foregoing Scherrer's Formula,
 25 more preferably 200 Å or less.

Observation of Crystal Structure

The crystal structure of the positive pole

THE UNIVERSITY OF CHICAGO

or

 δ

25 The dispersion angle and the dispersion intensity
obtainable in the X-ray small angle dispersion method
also enables ~~of~~ fluctuation of ununiform density

e

VI
2-

being

VI
o

being

VI
2

The positive pole is manufactured in such a manner that the bonding material, and conductive powder if necessary, is mixed with the powder of the compound of the transition metal and the group 6A element manufactured by the foregoing method, and then formed into the positive pole together with the collector. It is preferable that the foregoing forming process be

1 performed in dry air from which water has sufficiently
en be removed, more particularly ~~under~~ inactive gas in an
atmosphere.

5 The conductive powder acts to enhance the
electron conduction and facilitate the current
collection because the active material, which is the
compound of the transition metal and the group ~~IA~~ VI
element, does not substantially have the electron
conductivity.

10 The conductive powder may be carbon material,
such as acetylene black, ~~ketchen~~ black or graphite
powder, or metal, such as nickel, titanium, copper or
stainless steel. It is preferable that the mixture
ratio of the conductive powder with respect to the
15 positive pole active material be 1 or less.

20 The bonding material bonds the positive pole
active material powder to one another and prevents
generation of cracks in the charge and discharge cycle
to prevent the separation from the collector. The
bonding material may be one or more types of resin
which are stable against the organic solvent and which
d are selected from a ~~group~~ consisting of fluororesin,
polyethylene, polypropylene and silicon resin. It is e
preferable that the foregoing resin be in the form of
25 liquid or solution or having a low melting point. e
Further, it is preferable that the solvent be removed
and the resin is crosslinked during the process of

1 manufacturing the positive pole. As a result, the
content of the bonding material in the positive pole
can be lowered and the capacity of the battery can be
improved. The liquid resin or the resin which can be
5 dissolved in the solvent is exemplified by fluororesin
having an ether bond and silicon resin. If the
fluororesin having the ether bond is used, the
concentration can be lowered when it is dissolved in
a solvent. Therefore, the content in the positive pole
10 can be lowered as much as possible and the void ratio *porosity*
can be raised. Further, the state is very stable after
crosslinking has been performed so that a satisfactory
effect can be obtained upon the charge and discharge
cycle.

15 It is also preferable that dehydration is
performed with heat generated by microwaves and a
vacuum ~~dryer~~ *dryer* is used to dehydrate the positive pole
after the positive pole has been formed.

20 It is preferable that the mixture ratio of the
bonding material with respect to the positive active
material be 0.1 or less.

Examples

25 Examples of the present invention will now be
described. It should be noted that the present
invention is not limited to the examples below.

Example 1-1

A flat type battery having a simple structure,

1 exhibiting assembling easiness and having a cross-sectional structure schematically shown in Fig. 2 was assembled to evaluate the characteristics of the secondary battery while mainly evaluating the life
5 against cycle operation.

First, a solution in which colloidal silica manufactured by Shokubai Kasei and subjected to hydrophobic treatment in an atmosphere of dry argon gas was dispersed in N, N - dimethylformamide was dehydrated
10 by active alumina. Then, lithium metal foil to which titanium mesh collector 200 was pressed against the reverse side was immersed in the colloidal silica solution prepared by the foregoing method, and then dried at 120°C so that a lithium negative pole 201
15 covered with silica was manufactured.

A positive pole activating material 203 was manufactured in such a manner that a mixture of dehydrated and electrolyzed manganese dioxide and lithium carbonate was heated so that a lithium-manganese
20 composite oxide was prepared. Then, tetrafluoroethylene polymer powder was mixed, and then pressed against the titanium mesh as to be formed into a designed shape.

The electrolytic solution was obtained by dissolving, by 1 M (mol/l), lithium arsenate
25 hexafluoride salt in an equally mixed solvent of propylene carbonate (PC) and dimethoxyethane (DME).

A separator 208 was formed in such a manner that

The assembling process was performed in such a manner that the separator 208 was placed between the negative pole 201 and the positive pole 203 followed by inserting them into a positive pole case 207 made of titanium clad stainless steel. Then, an electrolytic solution was injected followed by sealing the positive pole case 207 with a negative cap 206 made of titanium clad stainless steel and an insulating packing 210 made of fluororubber so that a secondary battery was manufactured.

15 A lithium secondary battery was manufactured by
a method similar to Example 1-1 except for excluding
the surface covering treatment using the metal lithium
foil performed in Example 1-1.

20 A battery similar to that according to Example
1-1 was manufactured.

25 First, aluminum trichloride and phosphoric acid were allowed to react with each other in ethyl alcohol, and gradually heated to 100°C so that glass form

7/1/

1 aluminum phosphate was obtained. Then, it was dispersed
in n-hexane so that a film forming solution was
prepared. The film forming solution was applied to a
lithium metal foil to which the titanium mesh collector
5 was pressed. Then, a film was formed at 120°C. Then,
similar processes to those according to Example 1-1 were
performed so that a lithium battery was manufactured.

Example 1-3

A battery similar to that according to Example
10 1-1 was manufactured.

The preparation of the materials and assembly
were performed in an atmosphere of dry argon similarly
to Example 1-1.

First, acetic acid and water were added to an
15 ethyl alcohol solution of tetrabutoxytitanium to be
hydrolyzed. Then, diethylamine was added so that
colloidal titanium oxide was formed. Then, colloidal
titanium oxide was dissolved in a xylene solution of
polyethylene so that a film forming solution was
20 prepared. The film forming solution was applied to
the lithium metal foil to which the stainless mesh
collector was pressed followed by drying it at 100°C.
Then, electron beams were applied to crosslink the
polyethylene so that a film was formed. Then, similar
25 processes to those according to Example 1-1 were
performed so that a lithium battery was manufactured.

1 Example 1-4

A battery similar to that according to Example 1-1 was manufactured.

5 The preparation of the materials and assembly were performed in an atmosphere of dry argon similarly to Example 1-1.

20 A toluene solution of triethylaluminum was mixed with an isopropyl alcohol solution of tetrabutoxytitanium, followed by adding acetic acid and water⁴⁰ as to be hydrolyzed. Then, diethylamine was added so that colloidal titanium oxide-alumina was formed. Then, the colloidal titanium oxide-alumina was dispersed in a toluene solutionⁱⁿ which acrylic resin and epoxy resin were dissolved so that the film forming solution was prepared. The film forming solution was applied to a lithium metal foil to which the stainless mesh collector was pressed, and then a film was formed at 80°C. Then, similar processes to those according to Example 1-1 were performed so that a lithium battery was manufactured.

20 Example 1-5

A battery similar to that according to Example 1-1 was manufactured.

25 The preparation of the materials and assembly were performed in an atmosphere of dry argon similarly to Example 1-1.

First, acetic acid and water were added to an

1 ethyl alcohol solution of tetraethoxysilane^{as} to be ^{so}
hydrolyzed. Then, diethyl amine was added so that
colloidal silica oxide was formed. Then, the colloidal
silica was dispersed in an acetonitrile^{ile} solution of
5 polyethylene glycol, followed by adding
^{n/ile} azobisisobutyronitrile~~NA~~ and arsenic hexafluoride lithium
salt so that a film forming solution was prepared. The
film forming solution was applied to the lithium metal
foil to which the stainless mesh collector was pressed,
10 followed by drying it at 100°C^{so} as to crosslink
polyethylene glycol so that a film was formed. Then,
similar processes to those according to Example 1-1 were
performed so that a lithium battery was manufactured.

Example 1-6

15 A battery similar to that according to Example
1-1 was manufactured.

First, felt-shape carbon was immersed in silica
coating solution NT-G326, which was manufactured by
Nissan Kagaku and to which boron tetrafluoride lithium
20 salt was added, and taken out from it. Then, it was
hardened at 110°C for 20 minutes and 300°C for 30
minutes so that silica coating was performed. The
obtained felt-shape carbon covered with the silica was
used as the cathode and the lithium metal was used as
25 the anode in an electrolytic solution in which arsenic
hexafluoride lithium salt was, by 1 M (mol/l), dissolved
in an equal-quantity mixture solvent of propylene

1 carbonate and dimethoxyethane dehydrated sufficiently.
As a result, lithium was introduced and allowed to
adhere to the felt-shape carbon covered with silica so
that the negative pole 201 was manufactured.

5 Then, similar processes to those according to
Example 1-1 were performed so that a battery was
manufactured.

Example 1-7

A battery similar to that according to Example
10 1-1 was manufactured.

First, paste obtained by mixing zinc oxide
powder, metal zinc powder and water glass was injected
into foamed nickel (Celmet) manufactured by Sumitomo
Denko. Then, the material was hardened at 80°C for 20
15 minutes and 200°C for 30 minutes so that the negative
pole 201 was formed.

Then, paste obtained by mixing, with nickel
hydroxide, nickel powder, cobalt powder, carboxylic
methyl cellulose serving as the bonding material,
20 ethylene glycol and water was injected into the Celmet
manufactured by Sumitomo Denko. Then, it was dried and
pressed so that the positive pole 203 was formed.

The separator was formed in such a manner that
polypropylene film subjected to hydrophilic treatment
25 and having small apertures was sandwiched by unwoven
polyamide sheets. The electrolytic solution was a 30
wt% potassium hydroxide solution. The assembly was

1 performed similarly to Example 1-1 so that a nickel-zinc
secondary battery was manufactured.

Comparative Example 1-2

5 A nickel-zinc secondary battery was manufactured
by a method similar to Example 1-7 except that the
negative pole was manufactured by mixing polyethylene
serving as the bonding material and ethylene glycol in
place of the water glass.

Example 1-8

10 A battery having a structure similar to that
according to Example 1-1 was manufactured. However, a
positive pole case having small apertures for receiving
oxygen in air was employed.

15 The negative pole 201 was formed similarly to
that according to Example 1-7.

The positive pole 203 was formed in such a manner
that the positive catalyzer layer was formed by adding
manganese dioxide to active carbon, and a water-
repellant film made of polytetrafluoroethylene and
20 cellulose-type diffusion paper were stacked on the
positive catalyzer layer.

The separator 208 comprises a cellophane film,
while the electrolytic solution comprises a 30 wt%
potassium hydroxide solution.

25 The battery was assembled in such a manner that
the separator 208 was held between the negative pole 201
and the positive pole 203, followed by inserting them

1 into the positive pole case 207 having small apertures
for receiving oxygen in air and made of titanium clad
stainless steel. Then, the electrolytic solution was
injected, and sealing was performed by the negative cap
5 206 made of the titanium clad stainless steel and the
insulating packing 210 made of fluorine rubber so that
the air-zinc secondary battery was manufactured.

Comparative Example 1-3

10 An air-zinc secondary battery was manufactured by
a method similar to that according to Example 1-8 except
that the negative pole according to Comparative Example
1-2 was used.

Evaluation of Performance of Secondary Battery

15 The performance of lithium secondary batteries
according to Examples 1-1 to 1-6 and Comparative Example
1-1, the nickel-zinc secondary battery according to
Example 1-7 and Comparative Example 1-2, and the air-
zinc secondary battery according to Example 1-8 and
Comparative Example 1-3 was evaluated. The evaluation
20 was performed by a charge and discharge cycle test under
the following conditions with respect to the cycle life
of the batteries according to Comparative Examples 1-1,
1-2 and 1-3. The conditions for the cycle test were
made as follows: the charge and discharge was
25 performed by 0.2C (electric current which was 0.2
times capacity/time), pause for 30 minutes and a cut-off
voltage of 1.0V was applied. A charging/discharging

1 apparatus HJ-101M6 manufactured by Hokuto Electric was
used. The charge/discharge test was commenced at
discharge, the battery capacity was evaluated, ^{and as} the 7
quantity of the third discharge, and the cycle life
5 was evaluated 7 by the number of cycles when the battery
capacity had deteriorated to 60% or less.

The cycle life of each battery with respect to
the cycle life of the battery according to Comparative
Example 1-1 which was made to be 1 was as shown in

10 Table 1.

As can be understood from the results of
comparisons made between Examples 1-1 to 1-6 and
Comparative Example 1-1, between Example 1-7 and
Comparative Example 1-2 and between Example 1-8 and
15 Comparative Example 1-3, the cycle life can
considerably be lengthened due to use of the foil made
of the negative pole activating material according to
the present invention and arranged in such a manner
that the surface is covered with the film having an
20 inorganic glass structure through which lithium ions
can be passed.

1

Table 1

5

10

15

20

25

Secondary Battery Manufactured		Cycle Life according to the present invention
Example	Comparative Example	Cycle Life according to Comparative Example
Example 1-1	Comparative Example 1-1	2.5
Example 1-2	Comparative Example 1-1	2.0
Example 1-3	Comparative Example 1-1	1.5
Example 1-4	Comparative Example 1-1	1.5
Example 1-5	Comparative Example 1-1	3.0
Example 1-6	Comparative Example 1-1	3.4
Example 1-7	Comparative Example 1-2	1.5
Example 1-8	Comparative Example 1-3	2.0

1 Example 2-1

A flat battery which had a simple structure, which could be assembled simply and which had a cross-sectional shape schematically shown in Fig. 2 was assembled to evaluate the characteristics of the secondary battery while evaluating the cycle life.

First, a peroxide benzoyl was, in an atmosphere of dry argon gas, dissolved in a toluene solution of poly (2-vinyl naphthalene) manufactured by Aldrich Chemical Company, Inc. Then, a lithium metal foil to which the stainless mesh collector 200 was pressed from the reverse side was immersed in it. Then, heat treatment at 100°C was performed so that a lithium pole 201 covered with the poly (2-vinyl naphthalene) was manufactured.

The positive pole activating material 203 comprised a lithium-manganese composite oxide prepared by heat treatment subjected to a mixture of dehydrated electrolytic manganese dioxide and lithium carbonate and a graphite mixture. Then, tetrafluoroethylene polymer powder was mixed and then pressed against a titanium mesh as to be formed.

The electrolytic solution was prepared by dissolving, by 1 M (mol/l), arsenate hexafluoride lithium salt in an equal-quantity mixture solvent of propylene carbonate (PC) and dimethoxyethane (DME).

The separator 208 was formed by sandwiching

- 1 a separator made of propylene and having small apertures
by unwoven polypropylene sheets.

Comparative Example 2-1

- 5 A lithium secondary battery was manufactured by
a method similar to Example 2-1 except ~~for~~ that the α
metal lithium foil surface covering treatment according
to Example 2-1 was omitted.

Example 2-2

- 10 A battery similar to that according to Example
2-1 was manufactured.

The preparation of materials and assembling of
the battery were performed in an atmosphere of dry
argon similarly to Example 2-1.

- 15 First, 0.03 M azobisisobutyronitrile was added to n/i/e
h
a 5M tetrahydrofuran solution of 9-vinyl anthracene,
following by performing polymerization at 45°C so that
a polymer solution was obtained. Then, the polymer
solution was applied to lithium metal foil to which a
titanium mesh collector was pressed followed by drying
20 the polymer solution. Then, ultraviolet rays were
applied so that a lithium pole covered with the
polyvinyl anthracene film was manufactured. Then,
similar processes to those according to Example 2-1
were performed so that the lithium secondary battery
25 was manufactured.

Example 2-3

A battery similar to that according to Example

00070331 054774

h

1 2-1 was manufactured.

The preparation of materials and assembling of the battery were performed in an atmosphere of dry argon similarly to Example 2-1. .

5 First, 9, 10-an~~tr~~acene dipropionic acid and ethylene glycol of the same mol and a small quantity of zinc acetate were injected into a reaction chamber followed by dehydrating and condensing them at 200°C in an argon gas flow. Then, azobisisobut~~yl~~onitril^h was added, and the lithium metal foil to which a stainless steel mesh collector was pressed was immersed followed by taking out it. Then, it was heated to 100°C so that a film was formed on the surface of lithium. Then, similar processes to those according to Example 2-1
10 were performed so that the lithium secondary battery
15 was manufactured. ^{up. 1/1/e}

Example 2-4

A battery similar to that according to Example 2-1 was manufactured.

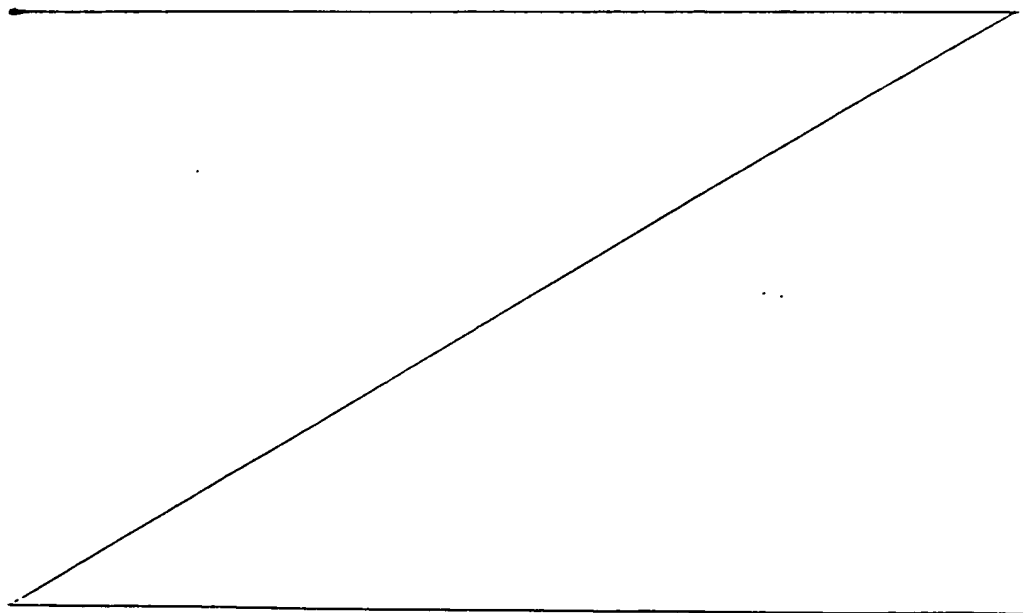
20 The preparation of materials and assembling of the battery were performed in an atmosphere of dry argon similarly to Example 2-1.

Tantalum pentachloride was dissolved in toluene at 80°C, and a toluene solution of 5, 12-bits
25 (phenylethynyl) naphthalene was added followed by polymerizing them at 80°C. An obtained polymer was cleaned with methyl alcohol, dried and again dissolved

1 in toluene so that a film forming solution was
prepared. Then, a lithium metal foil to which a
stainless steel mesh collector was pressed was
immersed, followed by raising it and drying the same.
5 Then, electron beams were applied to crosslink the
material so that a film was formed on the surface of
lithium. Then, similar processes to those according
to Example 2-1 were performed so that the lithium
secondary battery was manufactured.

10 Example 2-5

A lithium secondary battery similar to that
according to Example 2-1 was manufactured except that
peroxide benzoyl was dissolved in a toluene solution of
poly (2-vinyl naphthalene), and then arsenate
15 hexafluoride lithium salt was added so that the film
forming solution was prepared.



1 Example 2-6

A battery similar to that according to Example 2-1 was manufactured.

5 The preparation of materials and assembling of the battery were performed in an atmosphere of dry argon similarly to Example 2-1.

Felt-form carbon, which had been dehydrated and dried, was immersed in lithium dissolved in a stainless container, followed by cooling the same so that felt-form carbon was manufactured. Then, it was immersed in a toluene solution of poly (2-vinyl naphthalene) to which azobisisobutyronitrile was added, followed by raising the felt carbon. It was then dried at 80°C, irradiated with ultraviolet rays to be crosslinked so that the negative pole was manufactured. Then, similar processes to those according to Example 2-1 were performed so that the lithium secondary battery was manufactured.

Evaluation of Performance of Lithium Secondary Battery

20 The performance of lithium secondary batteries according to Examples 2-1 to 2-5 and Comparative Example 2-1 was evaluated. The evaluation was performed by a charge and discharge cycle test under the following conditions with respect to the cycle life of the batteries according to Comparative Example 2-1. The conditions for the cycle test were made as follows: the charge and discharge was performed by 0.2C (electric

1 current which was 0.2 times capacity/time), pause
for 30 minutes and a cut-off voltage of 1.0V was applied.
A charging/discharging apparatus HJ-101M6 manufactured
by Hokuto Electric was used. The charge/discharge
5 test was commenced at discharge, the battery capacity
was evaluated the quantity of the third discharge and
the cycle life was evaluated by the number of cycles
when the battery capacity had deteriorated to 60%
or less.

10 The cycle life of each battery with respect
to the cycle life of the battery according to Comparative
Example 1-1 which was made to be 1 was as shown in
Table 2.

As can be understood from the results of
15 comparisons made between Examples 2-1 to 2-5 and
Comparative Example 2-1, the cycle life can considerably
be lengthened due to use of the negative pole comprising
the lithium foil covered with the polymer of the
derivative of the aromatic hydrocarbon compound
20 according to the present invention.

1

Table 2

	Manufactured Lithium Battery	Cycle Life of Example / Cycle Life of Comparative Example
5	Comparative Example 2-1	1.0
	Example 2-1	3.0
	Example 2-2	1.5
	Example 2-3	2.0
	Example 2-4	3.0
10	Example 2-5	3.5
	Example 2-6	3.7

Example 3-1

A flat battery which had a simple structure,
15 which could be assembled simply and which had a cross
sectional shape schematically shown in Fig. 2 was
assembled to evaluate the characteristics of the
secondary battery while evaluating the cycle life.

First, a titanium mesh collector 200 was pressed
20 from the reverse side of the lithium metal foil in
an atmosphere of dry argon gas. Then, the lithium
metal foil was immersed in a dioxane solution of
tetrabutoxytitanium, followed by drying it so that
the lithium pole 201 having a film formed as described
25 above was manufactured.

The positive pole activating material 203
was prepared in such a manner that a mixture of a

1 dehydrated and electrolyzed manganese dioxide and
a lithium carbonate were heated so that a lithium-
manganese composite oxide was prepared. Then,
tetrafluoroethylene polymer powder was mixed, and
5 then it was pressed against a titanium mesh^{as} to
be formed as designed. i
AD

α/h
The electrolytic solution was prepared in
such a manner that arsenate hexafluoride lithium salt
was, by 1 M (mol/l) ^{1/2} was dissolved in an equal quantity
10 mixture solvent of propylene carbonate (PC) and
dimethoxyethane (DME).

The separator 208 was manufactured in such
a manner that a propylene separator having small
apertures was sandwiched by unwoven polypropylene
15 sheets.

Comparative Example 3-1

A battery similar to that according to Example
3-1 was manufactured except that the metal lithium
foil surface treatment was omitted.

20 Comparative Example 3-2

2
A battery similar to that according to Example
3-1 was manufactured.

The preparation of materials and assembling
of the battery were performed in an atmosphere of
25 dry argon similarly to Example 3-1. A solution in
which peroxide benzoyl was added to a hexane solution
of Tirano Coat (polytitanocarbosilane) manufactured

- 1 by Ube Kosan was applied to a lithium metal foil to
which a titan mesh collector was pressed, followed
by drying it. Then, it was heated to 80°C, and then
heated to 150°C so that a lithium pole having a Tirano
5 Coat film formed thereon was manufactured.

Then, similar processes to those according
to Example 3-1 were performed so that the lithium
secondary battery was manufactured.

Example 3-3

- 10 A battery similar to that according to Example
3-1 was manufactured.

The preparation of materials and assembling
of the battery were performed in an atmosphere of
dry argon similarly to Example 3-1.

- 15 First, 2, 4, 6-trimethyl-tris (3, 3, 3-
trifluoropropyl)cyclotrisiloxane was heated to 76°C
in an argon gas. Then, calcium silate catalyzer was
added and polymerization was performed so that a polymer
was obtained. Then, peroxide benzoyl was added to
20 the polymer, and then a lithium metal foil to which
the stainless steel mesh collector was pressed was
immersed in the solution, and rayed from the solution.
Then, heat treatment at 100°C was performed so that
a lithium pole having a polysiloxane film formed thereon
25 was manufactured.

Then, similar processes to those according
to Example 3-1 were performed so that the lithium

Example 3-4

5 The preparation of materials and assembling
of the battery were performed in an atmosphere of
dry argon similarly to Example 3-1.

Then, similar processes to those according
15 to Example 3-1 were performed so that the lithium
secondary battery was manufactured.

A battery similar to that according to Example 3-1 was manufactured.

A lithium secondary battery was manufactured similarly to Example 3-2 except that lithium was immersed in a solution in which arsenate hexafluoride lithium salt was added to a solution in which peroxide benzoyl was added to a hexane solution of Tirano Coat

- 1 (polytitanocarbosilane) manufactured by Ube Kosan.

Evaluation of Performance of Lithium Secondary Battery

- The performance of lithium secondary batteries according to Examples 3-1 to 3-5 and Comparative Example 5 3-1 was evaluated. The evaluation was performed by a charge and discharge cycle test under the following conditions with respect to the cycle life of the batteries according to Comparative Example 2-1. The conditions for the cycle test were made as follows:
- 10 the charge and discharge was performed by 0.2C (electric current which was 0.2 times capacity/time), pause for 30 minutes and a cut-off voltage of 1.0V was applied. A charging/discharging apparatus HJ-101M6 manufactured by Hokuto Electric was used. The charge/discharge 15 test was commenced at discharge, the battery capacity was ~~evaluated~~^{ass} the quantity of the third discharge and the cycle life was evaluate^d by the number of cycles when the battery capacity had deteriorated to 60% or less.

- 20 The cycle life of each battery with respect to the cycle life of the battery according to Comparative Example 1-1 which was made to be 1 was as shown in Table 3.

- As can be understood from the results of 25 comparisons made between Examples 3-1 to 3-5 and Comparative Example 3-1, the cycle life can considerably be lengthened due to use of the negative pole comprising

- 1 the lithium foil covered with the organic metal compound according to the present invention.

Table 3

5	Manufactured Lithium Battery	Cycle Life of Example / Cycle Life of Comparative Example
	Comparative Example 3-1	1.0
	Example 3-1	3.0
	Example 3-2	2.5
10	Example 3-3	1.5
	Example 3-4	2.0
	Example 3-5	3.0

Example 4-1

- 15 A flat battery which had a simple structure, which could be assembled simply and which had a cross sectional shape schematically shown in Fig. 2 was assembled to evaluate the characteristics of the secondary battery while evaluating the cycle life.

- 20 First, a titanium mesh collector 200 was pressed against the lithium metal foil from the reverse side in an atmosphere of dry argon. Then, the lithium metal foil was immersed in a teflon AF solution which was a copolymer of tetrafluoroethylene and 2, 2-

- 25 bistrifluoromethyl - 4, 5 - difluoro-1, 3 - dioxysol and which was manufactured by Dupont, ~~followed by~~
~~bring the lithium metal foil.~~ As a result, the lithium

1 negative pole 201 covered with amorphous fluororesin
was manufactured. The positive pole activating material
203 comprised a lithium-manganese composite oxide
prepared by heating a mixture of dehydrated and
5 electrolyzed manganese dioxide and lithium carbonate
and a mixture of graphite. Then, tetrafluoroethylene
polymer powder was mixed, and pressed against the
titanium mesh as to be formed as designed. The
electrolytic solution was prepared by dissolving,
10 by 1 M (mol/l), arsenate hexafluoride lithium salt
in an equal quantity mixture solvent of propylene
carbonate (PC) and dimethoxyethane (DME). The separator
208 was manufactured in such a manner that a propylene
separator having small apertures was sandwiched by
15 unwoven polypropylene sheets. The battery was assembled
in such a manner that the separator 208 was held
between the negative pole 201 and the positive pole
203, followed by inserting them into a positive pole
case 207 made of titanium clad stainless steel, followed
20 by injecting the electrolytic solution. Then, the
negative pole cap 206 made of the titanium clad
stainless steel and the insulating packing 210 made
of fluorine rubber were used for sealing so that the
lithium secondary battery was manufactured.

25 Comparative Example 4-1

A lithium secondary battery was manufactured
under the same conditions as those according to Example

1 4-1 except that the metal lithium foil surface covering
was omitted.

Example 4-2

A battery similar to that according to Example
5 4-1 was manufactured.

The preparation of materials and assembling
of the battery were performed in an atmosphere of
dry argon similarly to Example 4-1. The lithium metal
foil to which a titanium mesh collector was pressed
10 was inserted into a chamber of a sputtering apparatus,
and then retained gas was exhausted to a vacuum level
of 5×10^{-6} Torr. Then, argon gas was allowed to
flow to control the internal pressure to 3×10^{-3}
Torr, followed by performing RF discharge to generate
15 plasma for use in sputtering using Neoflon PFA which
was a copolymer of tetrafluoroethylene and perfluoro-
alkylvinyl ether and manufactured by Daikin as a target.
As a result, a lithium pole having a film formed thereon
was manufactured. Then, similar processes to those
20 according to Example 4-1 were performed so that the
lithium secondary battery was manufactured.

Example 4-3

A battery similar to that according to Example
2-1 was manufactured.

25 The preparation of materials and assembling
of the battery were performed in an atmosphere of
dry argon similarly to Example 4-1. The lithium metal

1 foil to which a stainless steel mesh collector was
pressed was inserted into a chamber of an RF (Radio
Frequency) plasma CVD apparatus, and then the retained
gas was exhausted to realize a vacuum level of 2 x
5 10^{-6} Torr. Then, vinylidene fluoride was introduced
into the chamber, and isobutyl vinyl ether was
introduced into the chamber while using hydrogen gas
as the carrier gas. While controlling the internal
pressure to 1 Torr, RF discharge was caused to take
10 place so that a plasma polymer film was formed on
the surface of lithium. Then, similar processes to
those according to Example 4-1 were performed so that
the lithium secondary battery was manufactured.

Example 4-4

15 A battery similar to that according to Example
4-1 was manufactured.

The preparation of materials and assembling
of the battery were performed in an atmosphere of
dry argon similarly to Example 4-1. A lithium secondary
20 battery was manufactured similarly to Example 4-1
except that the titanium mesh collector was pressed
from the reverse side, and then it was immersed in
a xylene solution of Lumiflon which was a copolymer
of tetrafluoroethylene and non-fluorine-type vinyl
25 ether, which was manufactured by Asahi Glass and to
which isocyanate and graphite powder were added. Then,
it was dried at 140°C for 10 minutes so that the lithium.

1 pole covered with the amorphous fluoro-resin was
manufactured.

Example 4-5

5 A battery similar to that according to Example
4-1 was manufactured.

The preparation of materials and assembling
of the battery were performed in an atmosphere of
dry argon similarly to Example 4-1. First, coating
fluoro-resin was prepared. An automatic crepe having *clave*
10 a stirring machine received 200 parts of pure water,
40 parts of vinyl fluoride, 60 parts of ethylvinyl
ether, 0.6 parts of perfluorocarboxylic acid, 0.2
parts of persulfuric ammonium and 3 parts of water.
Then, the solution was heated to 46°C while maintaining
15 the pressure at 42.5 atmosphere to perform polymerization
for 8 hours. An obtained polymer was cleaned with
hot methanol, followed by drying it. Then, it was
dissolved in tetrahydrofuran dehydrated sufficiently,
followed by adding peroxide benzoyl. Then, the lithium
20 metal foil to which a stainless steel mesh collector
was pressed was immersed followed by raising it. Then,
it was heated to 100°C so that a lithium pole covered
with fluoro-resin was manufactured.

Then, similar processes to those according
25 to Example 4-1 were performed so that the lithium
secondary battery was manufactured.

1 Example 4-6

A battery similar to that according to Example 2-1 was manufactured.

First, a lithium pole was manufactured. The
5 lithium metal foil to which a stainless steel mesh collector was pressed was injected into a vacuum chamber of a parallel and flat type plasma CVD apparatus to which a 13.56 MHz high frequency power source was connected in such a manner that it was placed perpen-
10 dicular to the parallel and flat electrode. Then, retained gas was exhausted to realize a vacuum level of 10^{-5} Torr. Then, 10 sccm of tetrafluoroethylene, 2 sccm of ethylene, 2 sccm of hydrogen, 1 sccm of helium and 1 sccm of oxygen were introduced into the
15 vacuum chamber, which was a reaction chamber, and then the internal pressure was maintained at 0.8 Torr. Then, 200 watts of high frequency power was supplied to the parallel and flat electrode so that a plasma polymer film of the fluororesin was formed on the
20 surface of lithium. By using the lithium pole covered with the fluororesin prepared by the foregoing method, so that a lithium secondary battery was manufactured by the similar processes to those according to Example 4-1.

25 Evaluation of Performance of Lithium Secondary Battery

The performance of lithium secondary batteries according to Examples 4-1 to 4-6 and Comparative Example

1 4-1 was evaluated. The evaluation was performed by
a charge and discharge cycle test under the following
conditions with respect to the cycle life of the
batteries according to Comparative Example 4-1. The
5 conditions for the cycle test were made as follows:
the charge and discharge was performed by 0.2C (electric
current which was 0.2 times capacity/time), pause
for 30 minutes and a cut-off voltage of 1.0V was applied.
A charging/discharging apparatus HJ-101M6 manufactured
10 by Hokuto Electric was used. The charge/discharge
test was commenced at discharge, the battery capacity
was evaluated the quantity of the third discharge and
the cycle life was evaluate, by the number of cycles
when the battery capacity had deteriorated to 60%
15 or less.

The cycle life of each battery with respect
to the cycle life of the battery according to Comparative
Example 4-1 which was made to be 1 was as shown in
Table 4.

20 As can be understood from the results of
comparisons made between Examples 4-1 to 4-6 and
Comparative Example 4-1, the cycle life can considerably
be lengthened due to use of the negative pole comprising
the lithium foil covered with the fluoro-resin having
25 the ether bond according to the present invention.

1

Table 4

5	Manufactured Lithium Battery	Cycle Life of Example	Cycle Life of Comparative Example 4-1
10	Comparative Example 4-1		1.0
	Example 4-1		3.5
	Example 4-2		1.5
	Example 4-3		2.0
	Example 4-4		3.0
	Example 4-5		2.5
	Example 4-6		1.5

Example 5-1

A flat battery which had a simple structure, which could be assembled simply and which had a cross sectional shape schematically shown in Fig. 2 was assembled to evaluate the characteristics of the secondary battery while evaluating the cycle life.

In an atmosphere of dried argon gas, the titanium mesh collecting pole 200 was pressed to the reverse side of the lithium metal foil. Then, the lithium metal foil was immersed in a tetrahydrofuran solution of Cryptofix 222 B Polymer which was a large ring compound polymer and which was manufactured by E. Merch. Then, it was dried and then heated to 150°C so that a lithium pole 201 covered with the large ring compound polymer was manufactured.

1 The positive pole activating material comprised
a lithium-manganese composite oxide prepared by heat
treatment applied to a mixture of dehydrated and
electrolyzed manganese dioxide and lithium carbonate
5 and a mixture of graphite. Then, tetrafluoroethylene
polymer was mixed, and then pressed against the
stainless steel mesh, as to be formed as designed.

20 The separator 208 was manufactured in such
a manner that a propylene separator having small
apertures was sandwiched by unwoven polypropylene
sheets.

25 The electrolytic solution was prepared by
dissolving, by 1 M (mol/l), arsenate hexafluoride
lithium salt in an equal quantity mixture solvent
of propylene carbonate (PC) and dimethoxyethane (DME).

Assembling of the battery were performed
similarly to Example 1-1.

Comparative Example 5-1

30 A lithium secondary battery was manufactured
similarly to Example 5-1 except that the metal lithium
foil surface covering was omitted.

Example 5-2

A battery similar to that according to Example
5-1 was manufactured.

35 The preparation of materials and assembling
of the battery were performed in an atmosphere of
dry argon similarly to Example 2-1. A lithium metal

10

Figure 1 consists of seven sub-diagrams labeled (a) through (g), arranged vertically. Each diagram shows a cross-section of a vortex structure. In (a), there is a single, elongated, shaded region representing a vortex filament. In (b), the filament begins to pinch at its center. In (c), the filament has pinched, forming two separate shaded regions. In (d), the two shaded regions are beginning to reconnect. In (e), the filaments have reconnected, forming a single, more compact shaded region. In (f), a small, dark, circular region (the vortex core) has formed within the shaded region. In (g), the final state is shown, with a well-defined vortex core and a surrounding filamentary structure.

Figure 1 consists of seven sub-diagrams labeled (a) through (g), arranged vertically. Each diagram shows a cross-section of a vortex structure. In (a), there is a single, elongated, shaded region representing a vortex filament. In (b), the filament begins to pinch at its center. In (c), the filament has pinched, forming two separate shaded regions. In (d), the two shaded regions are beginning to reconnect. In (e), the filaments have reconnected, forming a single, more compact shaded region. In (f), a small, dark, circular region (the vortex core) has formed within the shaded region. In (g), the final state is shown, with a well-defined vortex core and a surrounding filamentary structure.

Figure 1 consists of seven sub-diagrams labeled (a) through (g), arranged vertically. Each diagram shows a cross-section of a vortex structure. In (a), there is a single, elongated, shaded region representing a vortex filament. In (b), the filament begins to pinch at its center. In (c), the filament has pinched, forming two separate shaded regions. In (d), the two shaded regions are beginning to reconnect. In (e), the filaments have reconnected, forming a single, more compact shaded region. In (f), a small, dark, circular region (the vortex core) has formed within the shaded region. In (g), the final state is shown, with a well-defined vortex core and a surrounding filamentary structure.

Figure 1 consists of seven sub-diagrams labeled (a) through (g), arranged vertically. Each diagram shows a cross-section of a vortex structure. In (a), there is a single, elongated, shaded region representing a vortex filament. In (b), the filament begins to pinch at its center. In (c), the filament has pinched, forming two separate shaded regions. In (d), the two shaded regions are beginning to reconnect. In (e), the filaments have reconnected, forming a single, more compact shaded region. In (f), a small, dark, circular region (the vortex core) has formed within the shaded region. In (g), the final state is shown, with a well-defined vortex core and a surrounding filamentary structure.

clase

1 a polymer was obtained.

o/u

~~Tylenediisocyanate~~
Tylenediisocyanate was added to the thus-
obtained polymer, and then the lithium metal foil,
to which a titanium mesh collector was pressed, was
5 immersed. Then, the lithium metal foil was raised,
and then it was heated, and dried at 80°C so that
the surface of the lithium foil was covered with a
large ring compound polymer.

Then, similar processes to those according
10 to Example 5-1 were performed so that the lithium
secondary battery was manufactured.

Example 5-4

A battery similar to that according to Example
2-1 was manufactured.

15 The preparation of materials and assembling
of the battery were performed in an atmosphere of
dry argon similarly to Example 5-1. A lithium metal
foil, to which a titanium steel mesh collector was
pressed, was immersed in a toluene solution of 3, 3'-
20 dibenzyl - 1, 4, 8, 11 - tetraoxacyclotetradecan^c to
which azobisisobutylnitryl and arsenate hexafluoride
lithium salt were added. Then, the lithium metal
was raised from the solution, and then ultraviolet
rays were applied to crosslinking so that the surface
25 of the lithium metal foil was covered.

no/i/e

e

Then, similar processes to those according
to Example 5-1 were performed so that the lithium

1 secondary battery was manufactured.

Example 5-5

A battery similar to that according to Example 2-1 was manufactured.

5 The preparation of materials and assembling of the battery were performed in an atmosphere of dry argon similarly to Example 5-1. Styrene and 4, 7, 13, 16, 21, 24 - hexaoxa - 1, 10-diazobicyclo [8.8.8] hexa⁴oxa⁷sa¹n were dissolved in a tetrahydrofuran solution
10 of naphthalene degasified and dehydrated sufficiently. Then, graphite powder was mixed. The lithium metal foil, to which a titanium mesh collector was pressed, was immersed to perform polymerization reaction, followed by drying as to be hardened. As a result,
15 the surface of lithium was covered with a large ring compound polymer.

Then, similar processes to those according to Example 5-1 were performed so that the lithium secondary battery was manufactured.

20 Example 5-6

A battery similar to that according to Example 5-1 was manufactured.

The preparation of materials and assembling of the battery were performed in an atmosphere of
25 dry air.

A porous nickel sheet manufactured by Osaka Gas was dehydrated and dried as to be used as an anode,

c/e

so
F
B
I
O
T
E
C
H
N
I
C
A
S
S
E
T

1 while a platinum electrode was used as a cathode so
that electrolytic polymerization was performed in
an acetonitrile solution in which 0.1 M of benzo-18-
crown-6 and 0.2 M of boron tetrafluoride tetrabutylam-
5 monia salt were dissolved. As a result, a porous
nickel sheet covered with a crown ether polymer was
manufactured. Then, an electrolytic solution was
prepared in such a manner that 1M of boron tetrafluoride
lithium salt was dissolved in an equal-quantity mixture
10 solvent of propylene carbonate and dimethoxyethane.
An obtained porous nickel sheet thus covered was used
as a cathode and lithium metal was used as an anode.
Then, lithium was inserted between the porous nickel
sheet cover and the nickel as to be allowed to adhere
15 so that the negative pole 203 was formed.

Then, similar processes to those according
to Example 5-1 were performed so that the lithium
secondary battery was manufactured.

Example 5-7

20 A nickel-zinc battery having a similar
structure as that of the battery according to Example
5-1 was manufactured.

First, paste was prepared by mixing polyvinyl
alcohol, phthalocyanine zinc, zinc oxide powder, zinc
25 powder, formaldehyde, formic acid and water. The
paste was applied to a nickel mesh and heated so that
the negative pole 201 was manufactured.

1 Then, paste obtained by mixing nickel powder,
cobalt powder, carboxylic cellulose serving as a bonding
material, ethylene glycol and water with nickel
hydroxide was injected into foamed nickel (Celmet)
5 manufactured by Sumitomo Denko. Then, it was dried
and pressed so that a positive pole 203 was formed.

 The separator 208 was formed in such a manner
that a polyamide film subjected to hydrophilic treatment
and having small apertures was sandwiched by unwoven
10 polyamide sheets. The electrolytic solution was a
30 wt% potassium hydroxide solution. The assembly
was performed similarly to Example 5-1 so that a nickel-
zinc secondary battery was manufactured.

Comparative Example 5-2

15 A nickel-zinc secondary battery was manufactured
except that the negative pole 201 was formed by applying
paste obtained by mixing zinc oxide powder, zinc powder,
polyvinyl alcohol and ethylene glycol to the nickel
mesh followed by drying.

20 Example 5-8

 A battery having a structure similar to that
according to Example 5-1 was manufactured. However,
a positive pole case having small apertures for receiving
oxygen in air was used.

25 The negative pole 201 was manufactured in
such a manner that paste was applied to a nickel mesh
followed by heating to dry the negative pole 201,

1 the paste being obtained by mixing zinc oxide powder,
zinc powder, polyacrylamide, water, formaldehyde,
lithium hydroxide and phthalocyanine zinc.

5 The positive pole 203 was formed in such a
manner that a positive catalyzer layer was formed
by adding manganese dioxide to active carbon, and
a water/repellant film made of polytetrafluoroethylene
and cellulose dispersed paper were stacked on the
positive catalyzer layer.

10 The separator 209 comprised a cellophane film
and the electrolytic solution comprised 30 wt% solution
of potassium hydroxide.

Assembling was performed in such a manner
that the separator 208 was held between the negative
15 pole 201 and the positive pole 203, and they were
inserted into the positive pole case 207 having small
apertures for receiving oxygen in air and made of
titanium clad stainless steel. Then, the electrolytic
solution was injected and sealing was performed by
20 using the negative pole cap 206 made of titanium clad
stainless steel and the insulating packing made of
fluorine rubber. As a result, an air-zinc secondary
battery was manufactured.

Comparative Example 5-3

25 An air-zinc secondary battery was manufactured
similarly to Example 5-8 except that the negative
pole according to Comparative Example 5-2 was used.

1 Evaluation of Performance of Lithium Secondary Battery

(7)
The performance of lithium secondary batteries according to Examples 5-1 to 5-5 and Comparative Example 5-1 was evaluated. The evaluation was performed by
5 a charge and discharge cycle test under the following conditions with respect to the cycle life of the batteries according to Comparative Example 1. The conditions for the cycle test were made as follows: the charge and discharge was performed by 0.2C (electric
10 current which was 0.2 times capacity/time), pause for 30 minutes and a cut-off voltage of 1.0V was applied. A charging/discharging apparatus HJ-101M6 manufactured by Hokuto Electric was used. The charge/discharge test was commenced at discharge, the battery capacity
15 was evaluated the quantity of the third discharge and the cycle life was evaluated by the number of cycles when the battery capacity had deteriorated to 60% or less.

d

The cycle life of each battery with respect
20 to the cycle life of the battery according to Comparative Example 5-1 which was made to be 1 was as shown in Table 2.

As can be understood from the results of comparisons made between Examples 5-1 to 5-6 and
25 Comparative Example 2-1 and those between Example 5-7 and Comparative Example 5-3, the cycle life can considerably be lengthened due to use of the negative

1 pole comprising the lithium or zinc covered with the
large ring compound polymer according to the present
invention.

Table 5

5	Lithium Battery Manufactured		Cycle Life of Example / Cycle Life of Comparative Example
	Example	Comparative Example	
10	Example 5-1	Comparative Example 5-1	3.0
	Example 5-2	Comparative Example 5-1	2.5
	Example 5-3	Comparative Example 5-1	3.5
	Example 5-4	Comparative Example 5-1	4.0
15	Example 5-5	Comparative Example 5-1	3.0
	Example 5-6	Comparative Example 5-1	4.2
	Example 5-7	Comparative Example 5-2	2.8
	Example 5-8	Comparative Example 5-2	2.7
20			

Example 6-1

A flat battery which had a simple structure,
which could be assembled simply and which had a cross
25 sectional shape schematically shown in Fig. 2 was
assembled to evaluate the characteristics of the
secondary battery while evaluating the cycle life.

1 First, the titanium collector 200 was pressed against
the reverse side of the lithium metal foil in an
atmosphere of dry argon gas, and then the lithium
metal foil was immersed in a toluene solution PPZ-U1001
5 manufactured by Idemitsu. Then, it was previously
dried, and ultraviolet rays were applied so that the
lithium pole 201 covered with phosphazene was
manufactured.

10 The positive pole active material 204 was
prepared in such a manner that a lithium-manganese
composite oxide was prepared by heating a mixture
of dehydrated and electrolyzed manganese dioxide and
lithium carbonate. Then, tetrafluoroethylene polymer
powder was mixed followed by pressing to a titanium
15 mesh as to be formed as designed.

The electrolytic solution was prepared by
dissolving, by 1 M (mol/l), arsenate hexafluoride
lithium salt in an equal quantity mixture solvent
of propylene carbonate (PC) and dimethoxyethane (DME).

20 The separator 208 was manufactured in such a manner
that a propylene separator having small apertures
was sandwiched by unwoven polypropylene sheets.

Comparative Example 6-1

25 A lithium secondary battery was manufactured
similarly to Example 6-1 except that the surface
covering of the metal lithium foil was omitted.

10
15
20

First, hexachlorotriphosphazene was repeatedly degasified, melted and solidified, and then it was heated to 250°C as to be polymerized so that polydichlorophosphazene was obtained. Then, a

it was again dissolved in tetrahydrofuran so that a solution of poly [bis (phenylamino)phosphazene] was prepared. Then, the foregoing solution was applied to the lithium metal foil, to which a titanium mesh collector was pressed, followed by drying the solution.

Then, similar processes to those according to Example 6-1 were performed so that the lithium secondary battery was manufactured.

25

A battery similar to that according to Example 5-1 was manufactured. The preparation of materials

1 and assembling of the battery were performed in an
atmosphere of dry argon similarly to Example 6-1.
First, a benzene solution of polydichlorophosphazene
was, while being stirred, slowly dropped in a
5 tetrahydrofuran solution of sodium alkoxide of
trifluoroethanol, followed by heating and refluxing
it. Then, it was neutralized, filtered, cleaned with
water and ethyl alcohol, and again sedimented with
acetone and water, followed by drying. As a result,
10 polybis (trifluoroethoxy) phosphazene was obtained.
The acetone solution of the polyfluoro~~phosphazene~~^{ethoxy}phosphazene *eth*
was applied to the lithium metal foil, to which a
stainless steel mesh collector was pressed. Then,
it was dried^{ed} and then irradiated with electron beams
15 so that a lithium pole covered with polyphosphazene
was manufactured. Then, similar processes to those
according to Example 6-1 were performed so that the
lithium secondary battery was manufactured.

Example 6-4

20 A battery similar to that according to Example
5-1 was manufactured. The preparation of materials
and assembling of the battery were performed in an
atmosphere of dry argon similarly to Example 6-1.
First, sodium alkoxide of naphthalene ethanol was,
25 in dioxane, prepared from naphthalene ethanol and
sodium hydroxide. Then, tetra-n-butyl ammonia bromide
was added to the sodium alkoxide, and then a dioxane

1 solution of polydichlorophosphazene was added while
being dripped. The thus-obtained mixed was subjected
to a heating reactions at 80°C, and the solvent was
somewhat removed. Then, it was again sedimented with
5 tetrahydrofuran and water, and then it was refined,
followed by Soxhlet-extracting it. As a result,
polydiphenoxyphosphazene was obtained. Then,
azoisobutylnitrile was added to a tetrahydrofuran
solution of the obtained polymer. Then, the lithium
10 metal foil, to which a stainless steel mesh collector
was pressed, was immersed and raised from it followed
by drying it and subjecting to a heat treatment set
to 80°C. As a result, a lithium pole covered with
polyphosphazene was manufactured. Then, similar
15 processes to those according to Example 6-1 were
performed so that the lithium secondary battery was
manufactured.

Example 6-5

A battery similar to that according to Example 5-1 was manufactured. The preparation of materials and assembling of the battery were performed in an atmosphere of dry argon similarly to Example 6-1. A lithium secondary battery was manufactured similarly to Example 6-1 except that arsenate hexafluoride lithium salt was added to a toluene solution of PPZ-U1001 manufactured by Idemitsu, and then lithium was immersed in the thus-prepared solution.

1 Evaluation of Performance of Lithium Secondary Battery

The performance of lithium secondary batteries according to Examples 6-1 to 6-5 and Comparative Example 6-1 was evaluated. The evaluation was performed by

5 a charge and discharge cycle test under the following conditions with respect to the cycle life of the batteries according to Comparative Example 6-1. The conditions for the cycle test were made as follows: the charge and discharge was performed by 0.2C (electric

10 current which was 0.2 times capacity/time), pause for 30 minutes and a cut-off voltage of 1.0V was applied. A charging/discharging apparatus HJ-101M6 manufactured by Hokuto Electric was used. The charge/discharge test was commenced at discharge, the battery capacity

15 was evaluate^d the quantity of the third discharge and the cycle life was evaluate^d by the number of cycles when the battery capacity had deteriorated to 60% or less. The cycle life of each battery with respect to the cycle life of the battery according to Comparative

20 Example 6-1 which was made to be 1 was as shown in Table 6. As can be understood from the results of comparisons made between Examples 6-1 to 6-5 and Comparative Example 6-1, the cycle life can considerably be lengthened due to use of the negative pole comprising

25 the lithium or zinc covered with the large ring compound polymer according to the present invention.

1

Table 6

Manufactured Lithium Battery	Cycle Life of Example / Cycle Life of Comparative Example 2-1
Comparative Example 6-1	1.0
Example 6-1	2.0
Example 6-2	1.5
Example 6-3	2.0
Example 6-4	3.0
Example 6-5	2.5

Example 7-1

A flat battery which had a simple structure, which could be assembled simply and which had a cross sectional shape schematically shown in Fig. 2 was assembled. The preparation of materials and assembling of the battery were performed in an atmosphere of dry argon.

First, the titanium mesh collector 200 having a lead was pressed against the reverse side of the lithium metal foil in an atmosphere of dry argon. Then, it was immersed in a nitromethane solution of acetyl cellulose to which azobisisobutyronitrile and boron tetrafluoride lithium salt. Then, it was dried, and irradiated with ultraviolet rays so that a film was formed. As a result, the lithium negative pole 201 was manufactured.

n/n/k/e

1 The positive pole activating material was
prepared in such a manner that a lithium-manganese
oxide was prepared by mixing electrolyzed manganese
dioxide and lithium carbonate at a ratio of 1:0.4
5 and by heating the mixture at 800°C. Then, ket^{ch}en
black and Super Konak, which is a fluororesin paint
manufactured by Nihon Yushi were mixed to the prepared
lithium-manganese oxide. Then, it was pressed against
a nickel mesh, as to be formed as designed followed
10 by performing heat treatment set to 170°C. As a result,
the positive pole 203 was manufactured.

 The separator 208 was manufactured in such
a manner that a porous layer-shape alumina film, an
unwoven polypropylene sheet and polypropylene separator
15 having small apertures were sandwiched.

 The electrolytic solution was prepared by
dissolving, by 1 M (mol/l), tetrafluoride borate lithium
salt in an equal quantity mixture solvent of propylene
carbonate (PC) and dimethoxyethane (DME).

20 The assembly was performed in such a manner
that the negative pole 201, the positive pole 203
and the separator 208 were sandwiched, as to be inserted
into the positive pole case 207 made of titanium clad
stainless steel, and then the electrolytic solution
25 was injected. Then, sealing was performed by the
negative cap 206 made of the titanium clad stainless
steel and the insulating packing 210 made of fluorine

1 rubber so that a lithium secondary battery was
manufactured.

Example 7-2

A battery similar to that according to Example
5 7-1 and shown in Fig. 2 was manufactured.

The preparation of materials and assembling
of the battery were performed in an atmosphere of
dry argon similarly to Example 7-1.

A lithium secondary battery was manufactured
10 by a method similar to that according to Example 7-1.

First, the titanium mesh collector 200 having
a lead was pressed against the reverse side of the
lithium metal foil in an atmosphere of dry argon gas.
Then, it was immersed in a tetrahydrofuran solution
15 of a polyethylene oxide to which peroxide benzoyl
was added, and then it was dried at 110°C, and ultra-
violet rays were applied so that a film was formed.
As a result, the lithium negative pole 201 was
manufactured.

20 The positive pole activating material was
prepared in such a manner that a lithium-manganese
oxide was prepared by mixing electrolyzed manganese
dioxide and lithium carbonate at a ratio of 1:0.4
and by heating the mixture at 800°C. Then, ket~~chen~~
25 black and tetrafluoroethylene polymer powder were
mixed with the prepared lithium-manganese oxide. Then,
it was pressed against a nickel mesh_Λ as to be formed

j

AO

1 as designed followed by performing heat treatment
set to 250°C. As a result, the positive pole 203
was manufactured.



2 The separator 208 was manufactured by sandwiching
5 a unwoven polypropylene sheet and a polypropylene
separator having small apertures.

The electrolytic solution was prepared by
dissolving, by 1 M (mol/l), tetrafluoroborate lithium
salt in a solvent of propylene carbonate (PC).

10 Then, similar processes to those according
to Example 7-1 were performed so that the lithium
secondary battery was manufactured.

Example 7-3

A battery similar to that according to Example
15 7-1 and shown in Fig. 2 was manufactured.

The preparation of materials and assembling
of the battery were performed in an atmosphere of
dry argon similarly to Example 7-1.

20 First, the lithium surface film was manufactured
in such a manner that lithium foil to which the nickel
mesh collector 200 was pressed was placed in a sputtering
apparatus. Then, a degree of vacuum of 1.5×10^{-4}
pascal ^{was applied} by lowering the pressure and by degasifying
the inside of the sputtering apparatus. Then, argon
25 gas was introduced ^{at} by 5 sccm, and the internal pressure
in the film forming chamber was maintained at $6 \times$
 10^{-1} pascal to perform sputtering while using polyether

e 1 sulfon~~y~~ as a target so that the lithium negative pole
201 covered with chitosan having a thickness of 500 Å
was obtained. *poly ether sulfone*

Then, similar processes to those according
5 to Example 7-2 were performed so that the lithium
secondary battery was manufactured.

Example 7-4

(7) *A battery was manufactured*
Under the same conditions as those according
to Example 7-3 except in that lithium foil to which the
10 nickel mesh collector 200 was pressed was placed in
a sputtering apparatus. Then, a degree of vacuum
of 1.5×10^{-4} pascal *is applied* by lowering the pressure and
by degasifying the inside of the sputtering apparatus.

Then, argon gas was introduced *at* 5 sccm, and the internal
15 pressure in the film forming chamber was maintained
at 6×10^{-1} pascal to perform sputtering while using
chitosan as a target so that the lithium negative
pole 201 covered with chitosan having a thickness
of 1000 Å was obtained.

20 Then, similar processes to those according
to Example 7-2 were performed so that the lithium
secondary battery was manufactured.

Example 7-5

- /
A flat nickel-zinc secondary battery which
25 had a simple structure, which could be assembled simply
and which had a cross-sectional shape schematically
shown in Fig. 2 was manufactured.

AD

pile

The electrolytic solution comprised 30 wt% potassium hydroxide water solution to which lithium hydroxide was added.

Example 7-6

A flat nickel-zinc secondary battery which

1 had a simple structure, which could be assembled simply
and which had a cross/sectional shape schematically
shown in Fig. 2 was manufactured. ←

7
⑦
5 Under the same conditions as those according
to Example 7-5 except that the formed zinc negative
pole was placed in a sputtering apparatus, and the
inside pressure was lowered to a degree of vacuum
of 1.5×10^{-4} pascal by lowering and degasifying the
inside. Then, argon gas was introduced by 5 sccm, at
10 and the internal pressure in the film forming chamber
was maintained at 6×10^{-1} pascal. Then, sputtering
was performed while using collagen as a target so
that a zinc negative pole covered with collagen having
a thickness of 1000 \AA was obtained.

15 The positive pole 203 was manufactured by
impregnating nickel hydroxide into a sintered nickel
pole plate.

Then, similar processes to those according
to Example 2-1 were performed so that the nickel-
20 zinc secondary battery was manufactured.

In order to evaluate the performance of the
batteries according to the foregoing Examples, batteries
according to Comparative Examples were manufactured.

Comparative Example 7-1

25 A lithium secondary battery was manufactured
by a method similar to Example 7-2 except that the
surface of the metal lithium foil was not covered.

1 Comparative Example 7-2

A nickel-zinc secondary battery was manufactured by a method similar to Example 7-6 except that the surface of the zinc negative pole was not covered.

5 Evaluation of Performance of Lithium Secondary Battery

The performance of lithium secondary batteries and nickel-zinc secondary batteries according to Examples and Comparative Examples was evaluated. The evaluation was performed by a charge and discharge cycle test
10 under the following conditions with respect to the cycle life of the batteries according to Comparative Examples.

The conditions for the cycle test were made as follows: the charge and discharge was performed
15 by 0.2C (electric current which was 0.2 times capacity/time), pause for 30 minutes and a cut-off voltage of 1.0V was applied. A charging/discharging apparatus HJ-101M6 manufactured by Hokuto Electric was used. The charge/discharge test was commenced at discharge,
20 the battery capacity was ~~evaluated~~^{was} the quantity of the third discharge, and the cycle life was evaluated by the number of cycles when the battery capacity had deteriorated to 60% or less.

The cycle life of batteries according to Examples
25 of the present invention with respect to the cycle life of the batteries according to Comparative Examples which was made to be 1.0 was as shown in Table 7.

7-2-2-3-4-5-6-7-8-9-10-11-12-13-14-15-16-17-18-19-20-21-22-23-24-25-26-27-28-29-30-31-32-33-34-35-36-37-38-39-40-41-42-43-44-45-46-47-48-49-50-51-52-53-54-55-56-57-58-59-60-61-62-63-64-65-66-67-68-69-70-71-72-73-74-75-76-77-78-79-80-81-82-83-84-85-86-87-88-89-90-91-92-93-94-95-96-97-98-99-100

7.

1

Table 7

5	Lithium Battery Manufactured		Cycle Life of Example	Cycle Life of Comparative Example
	Example	Comparative Example		
	Example 7-1	Comparative Example 7-1		3.6
	Example 7-2	Comparative Example 7-1		1.7
	Example 7-3	Comparative Example 7-1		1.3
10	Example 7-4	Comparative Example 7-1		1.6
	Example 7-5	Comparative Example 7-2		1.8
	Example 7-6	Comparative Example 7-2		1.4

15

As can be understood from the results of comparisons made between Examples 7-1 to 7-4 and Comparative Example 7-1 and those between Example 7-5 and 7-6 and Comparative Example 7-2, the cycle life can

20 considerably be lengthened due to use of the secondary battery according to the present invention.

Example 8

A battery which had a simple structure, which could be assembled simply and which had a cross sectional shape schematically shown in Fig. 2 was manufactured.

First, an RF (Radio Wave Frequency) discharge plasma processing apparatus having a structure

-/

1 schematically shown in Fig. 6 was used to apply surface
treatment to a lithium negative pole. In an atmosphere
of dry argon gas, a nickel mesh collector was pressed
against the reverse side of the lithium metal foil.

5 In order to protect the surface of lithium, a polyester
film was interposed at the time of coiling them. The
coil-shape lithium foil 400 was mounted on a conveyance
roll 407 of the plasma processing apparatus, and then
the retained gas was exhausted to realize a degree

10 of vacuum of 2×10^{-6} Torr. Then, 20 sccm of nitrogen
gas and 10 sccm of argon gas were introduced to a
plasma processing chamber 405 through a gas introduction
pipe 406. While controlling the internal pressure
in the plasma processing chamber to 0.5 Torr, waves

15 having a high frequency of 13.56 MHz were supplied
by 200 watts to cause discharge to take place. Then,
a winding roll 408 was used to hold and take up the
protection film comprising the polyester film so that
the surface of lithium was plasma-treated. Then,

20 the lithium foil subjected to the plasma treatment
was cut so that a negative pole was manufactured.

⑦ A* The protection film to be interposed at the time of
the winding operation in the plasma process, a separator
for a battery may be used.

25 The positive pole activating material 203
was prepared in such a manner that a lithium-manganese
oxide was prepared by mixing electrolyzed manganese

1 dioxide and lithium carbonate at a ratio of 1:0.4
and by heating the mixture at 850°C. Then, graphite
and tetrafluoroethylene polymer powder were mixed
to the prepared lithium-manganese oxide. Then, it
5 was pressed against a nickel mesh, as to be formed *AD*
into a desired positive pole.

The electrolytic solution was prepared by
dissolving, by 1 M (mol/l), tetrafluoroborate lithium *u*
salt in an equal quantity mixture solvent of propylene
10 carbonate (PC) and dimethoxyethane (DME).

The separator 208 was manufactured in such
a manner that a polypropylene separator having small
apertures was sandwiched by unwoven polypropylene
sheets.

15 Example 9

A battery similar to that according to Example
8 and shown in Fig. 2 was manufactured.

The preparation of materials and assembling
of the battery were performed in an atmosphere of
20 dry argon similarly to Example 8.

A lithium secondary battery was manufactured
by a method similar to that according to Example 8.

First, a microwave discharge plasma processing
apparatus having a structure schematically shown in
25 Fig. 7 was used to apply surface treatment to a lithium
negative pole. In an atmosphere of dry argon gas,
a nickel mesh collector was pressed against the reverse

1 side of the lithium metal foil, and then disposed
on a sheet processing substrate holder 501 followed
by injecting them in a load chamber 508 of the
microwave discharge plasma processing apparatus. Then,
5 the retained gas in the load chamber 508 was exhausted
to realize a degree of vacuum of 1×10^{-6} Torr. Then,
a gate valve 509 was opened, and the substrate holder
was conveyed to the plasma processing chamber 502
and the gate valve 509 was closed. Then, 10 sccm
10 of carbon tetrafluoride gas and 5 sccm of hydrogen
gas were introduced into the plasma processing chamber
502 through the gas introduction pipe 504. While
controlling the internal pressure in the plasma proces-
sing chamber to 0.01 Torr, microwaves having a frequency
15 of 2.45 GHz were supplied by 100 watts through a wave
guide pipe 506 and a microwave introduction window
505 to cause discharge to take place. As a result,
the surface of lithium was plasma-processed. The
lithium foil plasma-processed was used as the negative
20 pole.

Then, similar processes to those according
to Example 8 were performed so that the lithium
secondary battery was manufactured.

Example 10

25 Under the same conditions as those according
to Example 9 except that 10 sccm of gas of nitrogen
trifluoride was, as the lithium surface treatment

10 to Example 8 except that 5 sccm of chlorine trifluoride
gas, 2 sccm of oxygen gas and 100 sccm of helium gas
were, as the lithium surface treatment gas, introduced
through the gas introduction pipe 504 in place of
the 5 sccm of chlorine trifluoride gas and 2 sccm
15 of oxygen gas. Then, the surface of lithium was
processed while omitting discharge.

Under the same conditions as those according

to Example 8 except that 5 sccm of chlorine trifluoride gas, 2 sccm of oxygen gas and 100 sccm of helium gas were, as the lithium surface treatment gas, introduced through the gas introduction pipe 504 in place of the 5 sccm of chlorine trifluoride gas and 2 sccm of oxygen gas. Then, the surface of lithium was processed while omitting discharge.

20 In order to compare and evaluate the performance
of the batteries according to the foregoing Examples,
the following comparative battery was manufactured.

A lithium secondary battery was manufactured similarly to Example 8 except that the metal lithium foil, to which the nickel mesh was pressed, was, as it is, used as the negative pole.

25 similarly to Example 8 except that the metal lithium foil, to which the nickel mesh was pressed, was, as
it is, used as the negative pole.

1 Evaluation of Performance of Secondary Battery

The performance of lithium secondary batteries according to Examples and Comparative Example was evaluated. The evaluation was performed by a charge
5 and discharge cycle test under the following conditions with respect to the cycle life of the batteries according to Comparative Example.

The conditions for the cycle test were made as follows: the charge and discharge was performed
10 by 0.2C (electric current which was 0.2 times capacity/time), pause for 30 minutes and a cut-off voltage of 1.0V was applied. A charging/discharging apparatus HJ-101M6 manufactured by Hokuto Electric was used. The charge/discharge test was commenced at discharge,
15 the battery capacity was evaluated the quantity of the third discharge and the cycle life was evaluated by the number of cycles when the battery capacity had deteriorated to 60% or less.

The cycle life of batteries according to Examples
20 of the present invention with respect to the cycle life of the battery according to Comparative Example which was made to be 1.0 was as shown in Table 8.

As can be understood from the results of comparisons made between Examples 8 to 11 and Comparative
25 Example 8, the cycle life can considerably be lengthened due to use of the secondary battery according to the present invention.

1 Table 8

5	Lithium Battery Manufactured	Cycle Life of Example / Cycle Life of Comparative Example 8
	Comparative Example 8	1.0
	Example 8	2.5
	Example 9	2.0
	Example 10	3.0
10	Example 11	1.7

Example 12

A liquid-rich test cell similar to the apparatus shown in Fig. 1 was used to conduct tests.

15 The preparation of materials and assembly of the battery were performed in an atmosphere of dry Ar. Lithium metal foil, to which a titanium collector was pressed, was inserted into the chamber of an RF plasma CVD apparatus. Then, the retained
20 gas was exhausted to realize a degree of vacuum of 2×10^{-6} Torr. Then, tetrafluoroethylene, ethylene, hydrogen, helium and oxygen were introduced into the chamber, and the internal pressure was maintained at 0.8 Torr. Then, high frequency power of 200 watts
25 was supplied to a parallel and flat electrode so that a plasma polymer film of fluoro-resin was formed on the foregoing sample to have a thickness of 100 Å.

1 Then, acetylene gas was, as raw material gas, introduced
into the chamber, and the pressure in the chamber
was controlled to 0.1 Torr, and then RF discharge
was performed so that a carbon film was formed on
5 the surface of lithium to have a thickness of 200
Å so that a sample negative electrode was manufactured
(see Fig. 9A).

The positive pole activating material was
prepared by heating a mixture of dehydrated and
10 electrolyzed manganese dioxide, lithium carbonate
and black lead. The lithium-manganese composite oxide
was mixed with tetrafluoroethylene polymer powder,
and then it was pressed against titanium mesh to be
formed into a desired positive pole.

15 The separator was manufactured by sandwiching
a polypropylene separator having small apertures and
unwoven polypropylene sheets.

The electrolytic solution was prepared by
dissolving 1 M of arsenate hexafluoride lithium salt
20 in an equal-quantity mixture solvent of propylene
carbonate and dimethoxyethane.

A lithium secondary battery was manufactured
as shown in Fig. 1.

Example 13

25 Under the same conditions as those according
to Example 12 except that lithium metal foil covered
with a plasma polymer film of fluorine resin was inserted

⑦

mm

sieve

ing

1 negative pole.

Example 15

A solution in which Lumifron, which was
fluororesin paint manufactured by Asahi Glass, and
5 lithium hexafluoride salt were dissolved was applied
to the surface of the separator, and then it was pressed.
A battery similar to that according to Example 12
was manufactured except that the separator was disposed
as shown in Fig. 9F.

10 Example 16

A battery was manufactured under the same
conditions as those according to Example 12 except
that black lead fiber having a specific area of 10
m²/g or more was paper-made and thus-obtained black
15 lead paper (having a thickness of 200 μm) was disposed
between the negative pole and the separator as shown
in Fig. 9B.

Example 17

The preparation of materials and assembling
20 of the battery were performed in an atmosphere of
dry argon. Lithium metal foil, to which a titanium
mesh collector was pressed, was inserted into the
chamber of an RF plasma CVD apparatus. Then, the
retained gas was exhausted to realize a degree of
25 vacuum of 2×10^{-6} Torr. A hexane solution of
acetylacetone complex of nickel was used as the material,
and it was bubbled with hydrogen gas as to be introduced

E
2

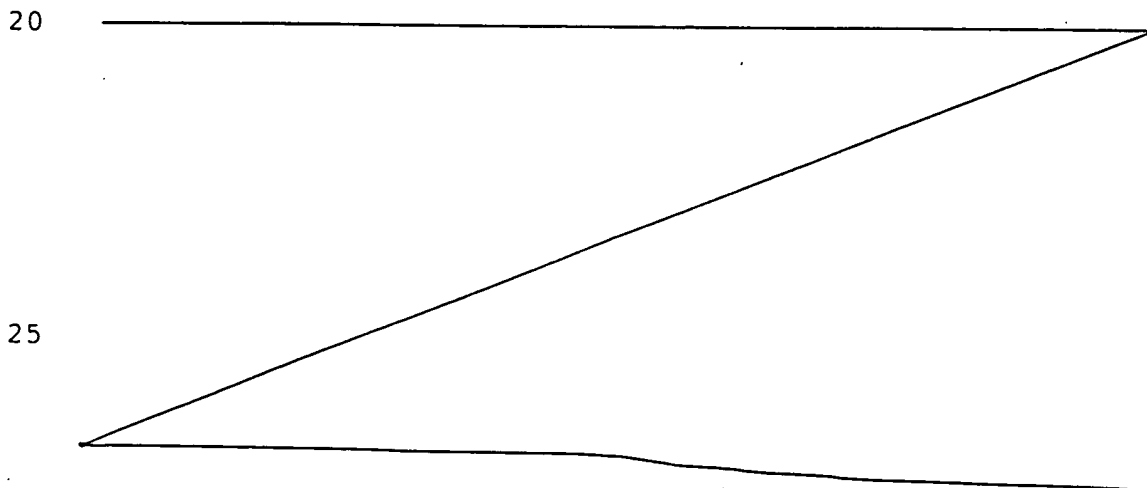
40

2025 RELEASE UNDER E.O. 14176

2/L
1 into the chamber. The pressure in the chamber was
controlled to 1 Torr, and RF discharge was performed
so that a nickel film was formed on the surface of
the metal foil to have a thickness of 200 Å, as to
5 ~~be served~~ as a sample pole. A battery was manufactured
under the same conditions as those according to ~~example~~ ⁴⁰
12 except that the foregoing sample pole was used ^E
as the negative pole.

Example 18

10 RF discharge was performed under the same
conditions as those according to Example 17 except
that oxygen gas was used as the material together
with the hexane solution of acetylacetonate complex
of nickel. As a result, a nickel oxide film was formed
15 on the surface of the lithium metal foil to have a
thickness of 50 Å to serve as a sample pole. A battery
was manufactured under the same conditions as those
according to ~~example~~ 12 except that the foregoing
sample pole was used as the negative pole.



1

15

Example 20

20

$$F_2$$

1 except that the foregoing sample pole was used as the
negative pole.

Example 21

5 A polypropylene separator was inserted into the
chamber of the RF plasma CVD apparatus. Then, the
retained gas was exhausted to realize a degree of
vacuum of 2×10^{-6} Torr. Acetylene gas was introduced
into the chamber, and then the pressure in the chamber
was controlled to 0.1 Torr and RF discharge was
10 performed. As a result, a carbon film was formed on
the surface of the separator to have a thickness of
200 Å. A battery was manufactured under the same
conditions as those according to ~~example~~ 12 except
that the foregoing separator was used and disposed as
15 shown in Fig. 9F.

Example 22

amorphous
A battery was manufactured
20 ~~atmosphere~~ *under the same conditions as those according*
to Example 21 except that monosilane gas was used as
the raw material gas to cover the separator with an
amorphous silicon film. A battery was manufactured
under the same conditions as those according to
example 12 except that the separator was used and
disposed as shown in Fig. 9F.

Example 23

25 The preparation of materials and assembling of
the battery were performed in an atmosphere of dry
argon. A polypropylene separator was inserted into

1 the chamber of the RF plasma CVD apparatus. Then, the
retained gas was exhausted to realize a degree of
vacuum of 10^{-5} Torr. Then, tetrafluoroethylene,
ethylene, H_2 , helium and oxygen were introduced into
5 the chamber, and the internal pressure was maintained
at 0.8 Torr. High frequency power was, by 200 watts,
supplied to a parallel and flat electrode so that a
plasma polymer film of fluororesin was formed on the
separator. Then, acetylene gas was, as the raw
10 material gas, introduced into the chamber, and the
internal pressure in the chamber was controlled to
0.1 Torr to perform RF discharge. As a result, a
carbon film was formed to have a thickness of 200 Å.
A battery was manufactured under the same conditions
15 as those according to ~~example~~ 12 except that the
foregoing separator was used and disposed as shown in
Fig. 9G.

Example 24

20 The preparation of materials and assembling of
the battery were performed in an atmosphere of dry
argon. A fluororesin film having micropores was
inserted into the chamber of the RF plasma CVD appara-
tus. Then, the retained gas was exhausted to realize
a degree of vacuum of 2×10^{-6} Torr. A hexane
25 solution of acetylacetone complex of nickel was, as
the raw material, used, as to be bubbled with hydrogen
gas as to be introduced into the chamber. The pressure

1 in the chamber was controlled to 1 Torr to perform RF
discharge so that a nickel film was formed on the
surface of the separator to have a thickness of 300 Å.
A battery was manufactured under the same conditions
5 as those according to ~~example~~ 12 except that the fore-
going film was used and disposed as shown in Fig. ~~9C~~. X

Example 25

10 *A battery was manufactured*
under the same conditions as those according to
Example 24 except that monosilane gas was used as the
raw material gas to form an amorphous silicon film on
the fluoro-resin film having micropores. *The* battery was
manufactured under the same conditions as those
according to ~~example~~ 12 except that the foregoing film
was used and disposed as shown in Fig. 9C.

15 Example 26

The preparation of materials and assembling of
the battery were performed in an atmosphere of dry
argon. Lithium metal foil, to which a titanium mesh
collector was pressed, was inserted into the chamber of
20 the RF plasma CVD apparatus. Then, the retained gas
was exhausted to realize a degree of vacuum of 2×10^{-6}
Torr. Monosilane gas and acetylene gas were, as the
raw material gas, introduced into the chamber, and then
the pressure in the chamber was controlled to 0.1 Torr
25 to perform RF discharge. As a result, the surface of
the lithium metal foil was covered with silicon carbide
film having a thickness of 300 Å to serve as a sample

1 pole. A battery was manufactured under the same
conditions as those according to ~~example~~ 12 except
that the foregoing sample pole was used as the negative
pole.

5 Example 27

The preparation of materials and assembling of
the battery were performed in an atmosphere of dry
argon. Lithium metal foil, to which a titanium mesh
collector was pressed, was inserted into the chamber
10 of the RF plasma CVD apparatus. Then, the retained
gas was exhausted to realize a degree of vacuum of
 5×10^{-6} Torr. Then, Ar gas was allowed to flow to
make the inside of the chamber to be an inactive
atmosphere. Then, the pressure in the chamber was
15 lowered to 3×10^{-3} Torr, and black lead and Si were
used as the target for use in the RF discharge.
Sputtering of Si was commenced at the initial stage of
the discharge and the proportion of black lead
sputtering was gradually raised so that a composite
20 layer of carbon and Si was formed on the surface of the
lithium metal foil to have a thickness of 300 Å to
serve as a sample pole. A battery was manufactured
under the same conditions as those according to ~~example~~
12 except that the foregoing sample pole was used as
25 the negative pole.

Example 28

A battery was manufactured under the same

1 conditions as those according to ~~example~~ 27 except E
2
that black lead, Si and polytetrafluoroethylene were
used as target and the thus-formed composite film was
stacked on the surface of the lithium metal foil.

5 Example 29

The preparation of materials and assembling of
the battery were performed in an atmosphere of dry
argon. The sample according to Example 12 was inserted
into the chamber of the RF plasma CVD apparatus. Then,
10 the retained gas was exhausted to realize a degree of
vacuum of 10^{-5} Torr. Then, tetrafluoroethylene,
ethylene, hydrogen, helium and oxygen were introduced
into the chamber, and the internal pressure was
maintained at 0.8 Torr. Then, high frequency power
15 was, by 200 watts, supplied to a parallel and flat
electrode to form a plasma polymer film of fluororesin
on the foregoing sample so that a sample pole was
obtained. A battery was manufactured under the same
conditions as those according to ~~example~~ 12 except E
20 that the foregoing sample pole was used as the negative
pole.

Example 30

The preparation of materials and assembling of
the battery were performed in an atmosphere of dry
25 argon. Lithium metal foil, to which a titanium mesh
collector was pressed, was inserted into the chamber
of sputtering apparatus. Then, the retained gas was

1 exhausted to realize a degree of vacuum of 5×10^{-6}
Torr. Ar gas was allowed to flow to make the inside of
the chamber to be an inactive atmosphere. Then,
pressure in the chamber was lowered to 3×10^{-3} Torr,
5 and black lead and LiAsF_6 were used as the targets to
perform RF discharge. As a result, carbon and LiAsF_6
were formed on the surface of the lithium metal foil
to have a thickness of 300 Å so that a sample pole was
obtained. A battery was manufactured under the same
10 conditions as those according to ~~example~~ 12 except
that the foregoing sample pole was used as the negative
pole.

Example 31

The separator according to Example 21 and
15 covered with carbon was used, and a fluoro-resin film
having micropores was stacked on the coated carbon as
shown in Fig. 9H. A battery was manufactured under
the same conditions as those according to ~~example~~ 12
except that the foregoing film was used.

20 Example 32

The spiral and cylindrical battery shown in
Fig. 3 was used in the test, the battery being ^qKR-A
type battery having a contour of 17.0 mm and 50.5 mm
high.

25 Paste obtained by, together with ethylene
glycol, kneading zinc oxide and metal zinc serving as
the main activating material and polyvinyl alcohol

1 serving as the bonding material was applied to an iron
plate applied with nickel plating having apertures.
Then, drying and pressing were performed so that a
zinc pole plate was obtained.

5 The zinc pole plate was inserted into the
chamber of the RF plasma CVD apparatus to perform RF
discharge in such a manner that the proportion of
tetrafluoroethylene was high in the initial stage of
the discharge process and the proportions of acetylene
10 and oxygen were raised in the following stage of the
discharge process. As a result, a fluororesin film
having a thickness of 200 Å was formed on the surface
of the zinc pole plate so that a sample pole was
obtained.

15 The positive pole plate was manufactured in
such a manner that paste was obtained by kneading a
solution in which nickel and cobalt were added to
nickel hydroxide and carboxydimethyl cellulose serving
as a bonding material, and water was added to the
20 kneaded solution. The paste was injected into foamed
metal (Celmet manufactured by Sumitomo Denko), and it
was dried and pressed.

A separator (Cell Guard manufactured by
Cellanese) was used which was manufactured by
25 integrating a film having small apertures and unwoven
polypropylene sheet.

The electrolytic solution comprised 30 wt%

1 potassium solution.

Assembly was performed in such a manner that a wound group in which a separator was interposed between the negative pole and the positive pole was
5 inserted into a battery case made of titanium clad stainless steel. Then, the electrolytic solution was injected, and the negative pole cap made of titanium stainless steel and an insulating packing made of fluorine rubber were inserted and they were caulked so
10 that a nickel-zinc secondary battery was manufactured.

Example 33

The flat type battery shown in Fig. 2 was used to conduct the test.

Tetrafluoroethylene polymer powder was mixed to
15 zinc oxide and metal zinc, and then was pressed against a nickel mesh, as to be formed into a zinc pole plate. The zinc negative pole was inserted into, *the*
chamber of the RF plasma CVD apparatus, and then fluororesin having a thickness of 50 Å and carbon
20 having a thickness of 200 Å were formed on the surface of the zinc pole plate so that a negative pole was formed.

- /
25 A positive pole catalyzer layer was formed by adding manganese dioxide to active carbon. Then, a water-repellant film made of polytetrafluoroethylene and dispersed paper made of cellulose were stacked on the positive pole catalyzer layer so that a positive

1 pole was formed. A separator made of cellophane and
30 wt% potassium hydroxide serving as the electrolytic
solution were employed.

Assembly was performed in such a manner that a separator was interposed between the negative pole and the positive pole and they were inserted into a battery case made of stainless steel and having small apertures. Then, the electrolytic solution was injected, and then a negative pole cap made of titanium clad stainless steel and an insulating packing made of fluorine rubber were used to perform sealing. As a result, an air-zinc secondary battery was manufactured.

Comparative Example 12

A battery was manufactured under the same conditions as those according to example 12 except that a negative pole, which comprised lithium metal foil having no carbon film, was used.

Comparative Example 13

A battery was manufactured under the same conditions as those according to example 31 except that a negative pole, which comprised a zinc pole plate which was not covered with the composite film of the fluoro-resin and carbon, was used.

Comparative Example 14

25 A battery was manufactured under the same conditions as those according to ~~e~~example 33 except that a negative pole, which comprised a zinc pole plate

1

5

10

15

20

25

the/s being

[illegible]

1. or the organic polymer (according to respective Examples).

Table 9

5	Manufactured Secondary Battery		Cycle Life of Example
	Examples	Comparative Examples	Cycle Life of Comparative Example
10	Example 12	Comparative Example 12	2.5
	Example 13	Comparative Example 12	2.1
	Example 14	Comparative Example 12	1.5
	Example 15	Comparative Example 12	1.3
	Example 16	Comparative Example 12	1.3
	Example 17	Comparative Example 12	2.2
	Example 18	Comparative Example 12	2.3
	Example 19	Comparative Example 12	2.0
15	Example 20	Comparative Example 12	2.1
	Example 21	Comparative Example 12	1.6
	Example 22	Comparative Example 12	1.5
	Example 23	Comparative Example 12	1.7
	Example 24	Comparative Example 12	1.5
	Example 25	Comparative Example 12	1.5
	Example 26	Comparative Example 12	2.2
	Example 27	Comparative Example 12	2.1
20	Example 28	Comparative Example 12	2.2
	Example 29	Comparative Example 12	2.0
	Example 30	Comparative Example 12	2.6
	Example 31	Comparative Example 12	1.6
	Example 32	Comparative Example 13	2.2
	Example 33	Comparative Example 14	2.2

Example 34

A polysiloxane film was formed by the following method.

1 As the film forming compound, 0.05 M (mol/l)
an amphipathic compound N-[b-(trimethylammonio)
ethyloxybenzoyl]-didodecyl-L-glutamic acid bromide
and 0.15 M of trimethoxymethyl silane were processed
5 with supersonic waves for 3 minutes as to be dispersed
in water. The dispersion solution was developed on
a tetrafluoroethylene polymer sheet (Goatex manufactured
by Japan Goa Tex) and allowed to stand at 25°C and 60%
relative humidity for 3 days so that a multi-layer
10 bimolecular film was obtained. The film was treated
with ammonia gas in a sealed glass container to
hydrolyze and condense the methoxysilane group. Ethyl
alcohol was used to extract and remove the amphipathic
compound so that a polysiloxane film was obtained on
15 the Goa Tex sheet.

Manufacturing of Secondary Battery

A lithium secondary battery which had a simple
structure, which could be assembled simply and which
had a cross sectional shape schematically shown in
20 Fig. 2 was manufactured.

The positive pole activating material 203 was
prepared in such a manner that electrolyzed manganese
dioxide and lithium carbonate were mixed at a ratio of
1:0.4, and then heated at 800°C so that a lithium-
25 manganese oxide was prepared. Then, graphite and
tetrafluoroethylene polymer powder were mixed to the
prepared lithium-manganese oxide, and then pressed

AD 1 against a nickel mesh, as to be formed into the positive pole.

Then, silica sol dispersion ethyl alcohol (manufactured by Shokubai Kasei) was mixed in water in which N-[b-(trimethylammonio)ethyloxybenzoyl]-didodecyl-L-glutamic acid bromide, which was the film forming compound, was dispersed. The positive pole was dipped in the foregoing dispersion solution, dried at room temperature, further dried at 80°C, and cleaned with hexane to remove the film forming compound. Then, it was dried at 250°C in a vacuum atmosphere so that the positive pole 203 covered with the multi-layer silica film was manufactured.

10
15 In an atmosphere of dry argon gas, titanium mesh collector 200 was pressed against the reverse side of the lithium metal foil, and then the lithium metal foil was immersed in a solution of Lumiflon, which was a copolymer of ethylene tetrafluoride and vinyl ether and which was manufactured by Asahi Glass, and then dried, as to be hardened. As a result, the lithium negative pole 201 covered with fluororesin was manufactured.

AD 20 The electrolytic solution was prepared by dissolving, by 1 M (mol/l), boron tetrafluoride lithium salt in an equal quantity mixture solvent of propylene carbonate (PC) and dimethoxyethane (DME).

The separator 208 comprised a composite member

1 of the polysiloxane film prepared as described above
and the Goa Tex sheet.

Assembly was performed in such a manner that
the separator 208 was interposed between the negative
5 pole 201 and the positive pole 203, as to be inserted *so*
into the positive pole case 207 made of titanium clad
stainless steel. Then, the electrolytic solution was *tr.*
injected, and then the negative pole cap 206 made of
titanium clad stainless steel and the insulating
10 packing 210 made of fluorine rubber were used to seal
so that a lithium secondary battery was manufactured.

Example 35

Preparation of Multi-Layer Metal Oxide

A titanium oxide was prepared by the following
15 method.

A film forming compound, that is,
dihexadecylphosphate was mixed to a sol dispersed
solution of very small particles of titanium oxide
(manufactured by Idemitsu), and dispersed with
20 ultrasonic waves similarly to Example 34. Then, it was
developed on a tetrafluoroethylene polymer membrane
filter. Then, it was dried at room temperature,
resulting in a cast film to be obtained which was then
cleaned with ethyl alcohol. Then, it was baked at
25 300°C so that a titanium oxide film was formed.

The separator 208 was manufactured in such a
manner that the thus-formed titanium oxide, unwoven

- 1 polypropylene sheets and a polypropylene separator
having small apertures were sandwiched.

A battery was manufactured under the same
conditions as those according to example 34 except the
5 foregoing arrangements.

E/for

Example 36

8
E
10 A lithium secondary battery was manufactured
under the same conditions as those according to
example 35 except that the titanium oxide film was
immersed in 0.1 % ethylalcohol solution of silane
coupling SH6020 (manufactured by Toray Dowconing).

(7)

Example 37

Preparation of Multi-Layer Metal Oxide

heated
15 A cast film obtained similarly to Example 35
was ~~baked~~ at 800°C so that an alumina film was
manufactured, the cast film being obtained from a film
forming compound brought into class four from N-(11-
bromoundecanoyl)-L-glutamic acid didodecylester with
triethyl amine and amorphous alumina super fine
20 particle sol.

The N-(11-bromoundecanoyl)-L-glutamic acid
didodecylester was prepared in such a manner that L-
glutamic acid didodecylester hydrochloride salt was
synthesized from L-glutamic acid and dodecylalcohol,
25 and then the L-glutamic acid didodecylester
hydrochloride salt, triethylamine, cyanophosphoric
acid diethyl and 11-bromoundecan acid were used.

1 Assembly of Secondary Battery

2 A nickel-zinc secondary battery which had a
3 simple structure, which could be assembled simply and
4 which had a cross~~/~~sectional shape schematically shown
5 in Fig. 2 was manufactured.

The positive pole was manufactured by
impregnating nickel hydroxide into a sintered nickel
pole plate.

6 The negative pole was formed in such a manner
7 that tetrafluoride ethylene polymer powder serving as
8 the bonding material was added to a mixture of zinc
9 powder and zinc oxide powder and they were pressed
10 against the two sides of a copper punching metal to
11 be formed into the desired shape. Then, alumina
12 trichloride and phosphoric acid were, in ethyl alcohol,
13 caused to react with each other at 0°C as to dip the
14 negative pole. Then, it was gradually heated up to
15 100°C so that glass-type aluminum phosphate film was
16 formed on the negative pole.

17 The electrolytic solution comprised 30 wt%
18 potassium hydroxide containing lithium hydroxide added
19 thereto.

The battery was assembled similarly to Example
34.

20 Example 38

21 A nickel-zinc secondary battery was manufac-
22 tured under the same conditions as those according

1 to Example 37 except that the surface of the negative
~~surface~~ was not covered with the aluminum phosphate.

pole
Example 39

5 A nickel-zinc secondary battery was manufac-
tured under the same conditions as those according to
Example 37 except that a positive pole manufactured
as follows was used.

A dispersion solution in which was mixed a
film forming compound obtained by bringing N-(11-
10 bromoundecanoyl)-L-glutamic acid didodecylester into
class four with triethylamine, amorphous alumina very
small particles sol and polyvinyl alcohol water
solution containing crosslinking material added thereto
was developed on the surface of the positive pole
15 formed by causing a sintered nickel plate to impregnate
nickel hydroxide, followed by drying the developed
solution. Then, crosslinking reactions were caused
to take place at 120°C, and clea^oed with ethyl alcohol. *n*
Then, the material was dried in a vacuum atmosphere so
20 that a positive pole covered with a composite film of
alumina and polyvinyl alcohol was manufactured.

In order to compare and evaluate the foregoing
batteries, the following comparative batteries were
manufactured.

25 Comparative Example 34

A lithium secondary battery was manufactured
under the same conditions as those according to

E 1 Example 35 except that no titanium oxide was used and
the lithium of the negative pole was not covered.

Comparative Example 35

E 5 A nickel-zinc secondary battery was manufac-
tured under the same conditions as those according to
Example 37 except that no alumina was used and zinc
of the negative pole was not covered.

Evaluation of Performance of Secondary Battery

10 The performance of lithium secondary batteries
according to Examples and Comparative Examples was
evaluated. The evaluation was performed by a charge
and discharge cycle test under the following condi-
tions with respect to the cycle life of the batteries
according to Comparative Examples.

15 The conditions for the cycle test were made as
follows: the charge and discharge was performed by
0.2C (electric current which was 0.2 times capacity/
time), pause for 30 minutes and a cut-off voltage of
1.0V was applied. A charging/discharging apparatus
20 HJ-101M6 manufactured by Hokuto Electric was used.
The charge/discharge test was commenced at discharge,
the battery capacity was ¹⁰⁵evaluated the quantity of the
third discharge and the cycle life was evaluate_d by
the number of cycles when the battery capacity had
25 deteriorated to 60% or less.

The cycle life of each battery with respect to
the cycle life of the battery according to Comparative

1 Examples which was made to be 1 was as shown in Table
2.

As can be understood from the results of
comparisons made between Examples 34 to 36 and
5 Comparative Example 34 and those between Examples 37
to 39 and Comparative Example 35, the cycle life can
be lengthened due to use of the secondary battery
having the structure according to the present invention.

Table 10

10

Secondary Battery Manufactured		Cycle Life of Example Cycle Life of Comparative Example
Example	Comparative Example	
Example 34	Comparative Example 34	5.4
Example 35	Comparative Example 34	2.1
Example 36	Comparative Example 34	2.3
Example 37	Comparative Example 35	2.6
Example 38	Comparative Example 35	1.9
Example 39	Comparative Example 35	2.2

15

20

Example 40

A lithium secondary battery which had a simple
structure, which could be assembled simply and which
25 had a cross-sectional shape schematically shown in
Fig. 2 was manufactured.

The positive pole activating material 203 was

1 manufactured in such a manner that electrolyzed
manganese dioxide and lithium carbonate were mixed at
a ratio of 1:0.4. Then, the mixture was heated to
800°C so that a lithium-manganese oxide was prepared.
5 Graphite and tetrafluoroethylene polymer powder were
added to the prepared lithium-manganese oxide, and
pressed against a nickel mesh¹ as to be formed into the
positive pole. AD

Then, the positive pole was immersed in a
10 solution of Teflon AF which was a copolymer of
tetrafluoroethylene and 2,2-bistrifluoromethyl-4,5-
difluoro-1, 3-dioxol and which was manufactured by
Dupont, and then it was dried. As a result, the
positive pole 203 covered with the fluororesin was
15 manufactured.

In an atmosphere of dry argon gas, the titanium
mesh collector 200 was pressed against the reverse
side of the lithium metal foil, and then the lithium
metal foil was immersed in a solution which was a
20 copolymer of ethylene tetrafluoride and vinyl ether and
which was manufactured by Asahi Glass. Then, it was
dried^A as to be hardened so that the lithium negative
pole 201 covered with the fluororesin was manufactured.

AD

The electrolytic solution was prepared by
25 dissolving, by 1 M (mol/l), boric acid tetrafluoride
lithium salt in an equal quantity mixture solvent of
propylene carbonate (PC) and dimethoxyethane (DME).

1 The separator 208 was manufactured in such a
manner that a polypropylene separator having small
apertures was sandwiched by unwoven polypropylene
sheets.

5 The assembly was performed in such a manner
that the separator 208 was held between the negative
pole 201 and the positive pole 203, as to be inserted 10
into the positive case 207 made of titanium clad
stainless steel. Then, the electrolytic solution was
10 injected, and then the negative pole cap made of
titanium clad stainless steel and the insulating
packing 210 made of fluorine rubber were used for
sealing so that a lithium secondary battery was
manufactured.

15 Example 41

A lithium battery was manufactured under the
same conditions as those according to example 40
except, the process for covering the positive pole.

for
20 The positive pole was manufactured similarly
to Example 40. Then, the positive pole was immersed
in an acetonitrile solution, in which were dissolved
0.1 M of monomer of benzo-15-crown-5 and 2.0 M of
electrolytic boronic acid tetrafluoride tetrabutyl
ammonium salt. Then, the platinum electrode was used
25 as the cathode pole, and voltage of 3 V was applied to
perform electrolysis and polymerization so that a
large ring compound polymer covering film was formed

ile

1 on the surface of the positive pole.

In an atmosphere of dry argon gas, the titanium mesh collector 200 was pressed against the lithium metal foil so that the negative pole was
5 manufactured.

Then, similar processes to those according to Example 40 were performed so that the lithium secondary battery was manufactured.

Example 42

10 A lithium secondary battery which had a simple structure, which could be assembled simply and which had a cross-sectional shape schematically shown in Fig. 2 was manufactured.

The positive pole was manufactured by a similar
15 process according to Example 40. Then, peroxide benzoyl and boronic acid tetrafluoride lithium were dissolved in a tetrahydrofuran solution of poly (2-vinyl naphthalene) manufactured by Aldrich Chemical Company, Inc. Then, the positive pole was immersed in
20 it, and then heated to 100°C so that the positive pole 203 covered with poly (2-vinyl naphthalene) was manufactured.

Then, similar processes to those according to Example 41 were performed so that the lithium secondary
25 battery was manufactured.

Example 43

The positive pole was manufactured by a process

1 similar to that according to Example 40. Then,
boronic acid tetrafluoride lithium salt was added and
dissolved in a toluene solution PPZ-U1001 manufactured
by Idemitsu. Then, the positive pole was immersed,
5 and previously dried, and then ultraviolet rays were
applied so that the positive pole 203 covered with
polyphosphazene was manufactured.

Then, similar processes to those according to
Example 41 were performed so that the lithium secondary
10 battery was manufactured.

Example 44

The positive pole was manufactured by a process
similar to that according to Example 40. The thus-
manufactured positive pole was injected into a
15 sputtering apparatus. Then, the retained gas was
exhausted to realize a degree of vacuum of 2×10^{-6}
Torr. Then, argon gas, which was a mixture of 10%
nitrogen gas and 5% acetylene gas, was allowed to flow.
The internal pressure was controlled to 3×10^{-3} Torr,
0 20 and lithium fluoride was made to be a target of
sputtering. As a result, the positive pole covered
with carbon and a film made of lithium nitride contain-
ing fluorine were formed.

Then, similar processes to those according to
25 Example 41 were performed so that the lithium secondary
battery was manufactured.

Example 45

1 A nickel-zinc secondary battery which had a
simple structure, which could be assembled simply
and which had a cross¹sectional shape schematically
shown in Fig. 2 was manufactured.

5 The positive pole was manufactured in such a
manner that ~~zinc~~ hydroxide was impregnated in a
nickel sintered nickel pole plate. Then, acetic acid and
water were added to an ethyl alcohol solution of
tetraethoxy silane to be dehydrated. Then, diethylamine
10 was added so that colloidal silica was formed. Then,
the positive pole was immersed in the colloidal
solution of the silica, and dried at 100°C. As a
result, a silica film was formed on the surface of the
positive pole.

15 The negative pole was manufactured in such a
manner that ethylene tetrafluoride polymer powder
serving as a bonding material was added to a mixture of
zinc powder and zinc oxide powder, then they
were pressed to the two sides of a copper punching metal
20 as to be formed into the negative pole.

The electrolytic solution comprised 30 wt%
potassium hydroxide water solution to which lithium
hydroxide was added.

The battery was assembled similarly to
25 Example 40.

In order to compare and evaluate the perform-
ance of the batteries according to Examples, the

1 following comparative batteries were manufactured.

Comparative Example 40

A lithium secondary battery was manufactured under the same conditions as those according to example
5 40 except that the positive pole and the negative pole were not covered.

Comparative Example 41

A nickel-zinc secondary battery was manufactured under the same conditions as those according to
10 example 45 except that the surface coating was omitted.

Evaluation of Performance of Secondary Battery

The performance of the secondary batteries according to Examples and Comparative Examples was evaluated. The evaluation was performed by a charge
15 and discharge cycle test under the following conditions with respect to the cycle life of the batteries according to Comparative Examples. The conditions for the cycle test were made as follows: the charge and discharge was performed by 0.2C (electric current
20 which was 0.2 times capacity/time), pause for 30 minutes and a cut-off voltage of 1.0V was applied. A charging/discharging apparatus HJ-101M6 manufactured by Hokuto Electric was used.

The charge/discharge test was commenced at
25 discharge, the battery capacity was evaluated as the quantity of the third discharge, and the cycle life was evaluated by the number of cycles when the battery

?

d

1 capacity had deteriorated to 60% or less.

The cycle life of each battery with respect to the cycle life of the battery according to Comparative Examples which was made to be 1 was as shown in Table 11.

As can be understood from the results of comparisons made between Examples 40 to 44 and Comparative Example 11 and those between Example 45 and Comparative Example 41, the cycle life can be lengthened due to use of the secondary battery having the structure according to the present invention.

Table 11

Secondary Battery Manufactured		Cycle Life of Example
Example	Comparative Example	Cycle Life of Comparative Example
Example 40	Comparative Example 40	5.1
Example 41	Comparative Example 40	2.0
Example 42	Comparative Example 40	1.4
Example 43	Comparative Example 40	1.6
Example 44	Comparative Example 40	1.8
Example 45	Comparative Example 41	1.7

25 Preparation of Positive Pole Activating Material

Methods of preparing the positive pole activating material according to the present invention are

1 exemplified in Preparation Methods 46 to 55 and the
conventional preparation methods are exemplified by
Comparative Preparation Methods.

Preparation Method 46

5 A lithium-manganese oxide was prepared as
follows.

Manganese acetate was dissolved in water, and
then super fine nickel powder ENP-005 manufactured by
Sumitomo Denko was suspended in a water solution of
10 manganese nitrate. Then, a water solution of lithium
hydroxide was dripped until the pH was 8 or higher
while vibrating the suspension solution with supersonic
vibrations of 20 kHz so that sedimentation was gener-
ated. Then, ethyl alcohol was added, and supernatant
15 liquid of the solution including the sediment was
removed by decantation. The ethylalcohol cleaning
and the decantation were repeated. Then, it was
dissolved in 0.1% methyl alcohol solution of Sila Ace
S210 (vinylmethoxysilane) which was a silane coupling
20 material manufactured by Chisso. Then, the solvent
was removed by a centrifugal separator. The obtained
sedimentation was dried at 120°C, and dried at 200°C
in a vacuum drier so that grains of manganese oxide
were prepared.

25 The size of crystal grains was measured from
the half value width of the X-ray analysis curve with
respect to a manganese oxide and the angle of

1 diffraction in accordance with the Scherrer's
Equation. The size of the crystal grain was 60 Å or
larger.

The RHEED pattern resulted in a ring pattern
5 like a halo pattern.

The X-ray radial distribution function
resulted in a continuous and moderate peak curve.

The scattering angle and the scattering
intensity obtainable from the X-ray small angle
10 scattering method resulted in non-uniform density
fluctuation to be observed.

The specific area was measured by the BET
method, resulting in that the specific area was 123
m²/g.

15 Preparation Method 47

Vanadium oxide was prepared as follows.

Vanadium pentaoxide was gradually added to a
water solution of lithium hydroxide, as to be dissolved. *AO*
While applying supersonic vibrations, the water
20 solution was sprayed into liquid nitrogen, as to be *AO*
frozen. Then, the temperature was raised to -20°C,
and the pressure was lowered so that freezing and
drying were performed to dehydrate and dry the material.
Obtained grains were dried at 150°C, and further
25 dried in a vacuum drier at 250°C so that grains of
vanadium oxide were obtained. Then, the sample was
immersed in 0.1 % isopropylalcohol solution of

1 tetra-iso-propoxytitanium, and then the solvent was
remove by a centrifugal separator. The obtained
sedimentation was dried at 120°C, and then dried at
200°C in a vacuum state so that grains of manganese
5 oxide were prepared.

Although the size of crystal grains was
intended to measure from the half value width of the
X-ray analysis curve and the angle of diffraction in
accordance with the Scherrer's Equation, it could not
10 be measured because the diffraction curve resulted in
a broad form.

The RHEED pattern resulted in a halo pattern.

The X-ray radial distribution function resulted
in a continuous and moderate peak curve.

15 The scattering angle and the scattering
intensity obtainable from the X-ray small angle
scattering method resulted in non-uniform density
fluctuation to be observed.

The specific area was measured by the BET
20 method, resulting in that the specific area was 105
m²/g.

Preparation Method 48

A lithium-nickel oxide was prepared as follows.

Nickel acetate was dissolved in a mixture
25 solvent of acetic acid, ethyl alcohol and water.
While vibrating the solution with supersonic vibra-
tions of 20 kHz, an ethyl alcohol solution of

1 ethoxylithium, which was alkoxide, was dripped as to
be mixed. Then, the solution was heated to 80°C
to enhance the hydrolysis decomposition reactions
so that sol was generated. The supernatant liquid of
5 the solution including the sol-shape sedimentation
was removed by decantation, cleaned with ethyl
alcohol, the decantation was repeated and the solvent
was removed by a centrifugal separator. The obtained
sedimentation was dried at 150°C, and then suspended
10 in a non-electrolyzed nickel plating solution Ni-701
manufactured by Kojundo Kagaku. Then, it was heated
to 70°C, nickel coating was performed, and water
cleaning and decantation were repeated. Then, ethyl
alcohol cleaning was performed, and decantation was
15 repeated, and then the solvent was removed by a
centrifugal separator. The sample was dried at 230°C
in a vacuum state so that grains of nickel oxide were
obtained.

Although the size of crystal grains was
20 intended to measure from the half value width of the
X-ray analysis curve and the angle of diffraction in
accordance with the Scherrer's Equation, it could not
be measured because the diffraction curve with respect
to an oxide resulted in a broad form.

25 The RHEED pattern resulted in a ring pattern
considered due to nickel plating. The pattern
before the nickel plating process resulted in a halo

1 pattern.

The X-ray radial distribution function resulted in a continuous and moderate peak curve. The scattering angle and the scattering intensity obtain^{able}

5 nable from the X-ray small angle scattering method resulted in non-uniform density fluctuation to be observed.

The specific area was measured by the BET method, resulting in that the specific area was 210
10 m²/g.

Preparation Method 49

A lithium-nickel-cobalt oxide was prepared by the following method.

Nickel nitrate and cobalt nitrate were
15 dissolved in water, and then a water solution of lithium hydroxide was dripped to a solution of the nickel nitrate and cobalt nitrate while vibrating with supersonic vibrations of 20 kHz until the pH was 8 or higher so that sedimentation was generated. Then,
20 ethyl alcohol was added so that the supernatant liquid of the solution including the sedimentation was removed by decantation. the ethyl alcohol cleaning and the decantation were repeated and the solvent was removed by a centrifugal separator. The obtained sedimentation was dried at 120°C, dried at 200°C in a vacuum state so that grains of a nickel cobalt oxide were prepared.

i/then
25

5

1

i

10

15

P

f

20

AD
AD

1 liquid of the solution including the sedimentation was
removed by decantation. The ethyl alcohol cleaning
and the decantation were repeated and the solvent
was removed by a centrifugal separator. The obtained
5 sedimentation was ~~dried~~ at 120°C, ~~dried~~ at 200°C in *then*
a vacuum state so that grains of a vanadium oxide were
prepared.

The size of crystal grains was measured from
the half value width of the X-ray analysis curve and
10 the angle of diffraction in accordance with the
Scherrer's Equation. The size of the crystal grain
was 80 Å.

The RHEED pattern resulted in a ring pattern
like a halo pattern.

15 The X-ray radial distribution function resulted
in a continuous and moderate peak curve.

The scattering angle and the scattering
intensity obtainable from the X-ray small angle
scattering method resulted in non-uniform density
20 fluctuation to be observed.

The specific area was measured by the BET
method, resulting in that the specific area was 100
m²/g.

Preparation Method 51

25 Vanadium-molybdenum oxide was prepared by the
following method.

The vanadium oxide and the molybdenum oxide

1 were mixed at a ratio of 7:3, and heated up to 800°C¹ 40
as to be melted and mixed so that a molten bath was
made. Then, the molten bath was dispersed by jet gas
which was a mixture of 20% oxygen and 2% hydrogen with
5 argon gas. It was sprayed at high speed to a cooled
and retaining metal disc so that grains of vanadium
oxide and molybdenum oxide were prepared.

The size of crystal grains was measured from
the half value width of the X-ray analysis curve and
10 the angle of diffraction in accordance with the
Scherrer's Equation. The size of the crystal grain
was 110 Å.

The RHEED pattern resulted in a ring pattern
having weak intensity.

15 The X-ray radial distribution function resulted
in a continuous and moderate peak curve.

The scattering angle and the scattering
intensity obtainable from the X-ray small angle
scattering method resulted in non-uniform density
20 fluctuation to be observed.

The specific area was measured by the BET
method, resulting in that the specific area was 60
m²/g.

Preparation Method 52

25 Titanium sulfide was prepared by the following
method.

Hydrogen gas was allowed to flow ~~by~~ 500 sccm

at

so 1 into a reaction chamber of a plasma CVD apparatus
degasified~~gas~~ to be ^{ing} vacuum state. The pressure was
maintained at 10 Torr and discharge was caused to take
place at a high frequency wave of 13.56 MHz. Then,
5 200 sccm of helium gas was, as a carrier gas, bubbled
in a hexane solution of tetrabutoxytitanium, and
at injected ~~by~~ 200 sccm through a nozzle into the
reaction chamber of the plasma CVD apparatus.
Simultaneously, 250 sccm of hydrogen sulfide was
so 10 introduced~~gas~~ to be reacted in a gas phase to capture
grains of titanium sulfide by a capturing machine.

TE 200 400 600 800 1000 1200 1400 1600 1800 2000 2200 2400 2600 2800 3000 3200 3400 3600 3800 4000 4200 4400 4600 4800 5000 5200 5400 5600 5800 6000 6200 6400 6600 6800 7000 7200 7400 7600 7800 8000 8200 8400 8600 8800 9000 9200 9400 9600 9800 10000

15 The size of crystal grains was measured from
the half value width of the X-ray analysis curve and
the angle of diffraction in accordance with the
Scherrer's Equation. The size of the crystal grain
was 200 Å.

The RHEED pattern resulted in a ring pattern
having weak intensity.

20 The X-ray radial distribution function resulted
in a continuous and moderate peak curve.

The scattering angle and the scattering
intensity obtainable from the X-ray small angle
scattering method resulted in non-uniform density
fluctuation to be observed.

25 The specific area was measured by the BET
method, resulting in that the specific area was 175
m²/g.

1 Preparation Method 53

Lithium-iron-cobalt oxide was prepared by the following method.

A mixture solution of 0.5 mol/l cobalt chloride
5 and 1 mol ferric chloride mixed at a ratio of 1:1 was gradually added to a 5 mol/l water solution of lithium hydroxide while stirring and bubbling argon gas. Then, reaction chamber was set to 100°C to be matured. After the maturation, it was injected into cooled
10 water, and cleaning was performed with water cooled by water by means of decantation until the pH of the solution was 8. It was dried at 200°C in a vacuum state, and crushed by a ball mill in an atmosphere of argon gas.

15 The size of crystal grains was measured from the half value width of the X-ray analysis curve and the angle of diffraction in accordance with the Scherrer's Equation. The size of the crystal grain was 150 Å.

20 The RHEED pattern resulted in a ring pattern having weak intensity to be observed.

The X-ray radial distribution function resulted in a continuous and moderate peak curve.

The scattering angle and the scattering
25 intensity obtainable from the X-ray small angle scattering method resulted in non-uniform density fluctuation to be observed.

1 The specific area was measured by the BET
method, resulting in that the specific area was 2100
m²/g.

Preparation Method
Example 54

5 Manganese acetate, magnesium chloride and urea
were added to a solution in which 300 g of vanadium
pentoxide was dissolved in 2 liters of hydrochloric
acid, followed by heating the solution to 95 to 95°C
for 10 minutes to generate ammonia. Lithium hydride
10 solution was dripped to make the pH to generate
sediment. Then, decantation and water cleaning were
repeated, and then cleaning with ethyl alcohol was
performed, and the material was dried by a spray
dryer. Then, the sample was dried at 200°C in a vacuum
15 state.

20 The size of crystal grains was measured from
the half value width of the X-ray analysis curve and
the angle of diffraction in accordance with the
Scherrer's Equation. The size of the crystal grain
was 90 Å.

 The RHEED pattern resulted in a ring pattern
like a halo pattern.

 The X-ray radial distribution function resulted
in a continuous and moderate peak curve.

25 The scattering angle and the scattering
intensity obtainable from the X-ray small angle
scattering method resulted in non-uniform density

1 fluctuation to be observed.

The specific area was measured by the BET method, resulting in that the specific area was $80 \text{ m}^2/\text{g}$.

5 Preparation Method 55

A lithium-copper-cobalt oxide was prepared by the following method.

ANALYST
y

10 An oxalic acid was added to a water solution in which a copper sulfate and a cobalt nitrate were dissolved. Then, supersonic vibrations were applied, and lithium hydroxide was dripped until the pH was 7 so that sedimentation was generated. Water cleaning and decantation were repeated, and then a water solution of lithium hydroxide was added, supersonic
15 vibrations were applied, and an ethyl alcohol was added. Decantation and cleaning with ethyl alcohol were repeated, and the material was dried by using a spray dryer. Further, the material was dried at 200°C in a vacuum state.

20 The size of crystal grains was measured from the half value width of the X-ray analysis curve and the angle of diffraction in accordance with the Scherrer's Equation. The size of the crystal grain was 160 \AA .

25 The RHEED pattern resulted in a ring pattern having weak intensity.

The X-ray radial distribution function resulted

in

1 a continuous and moderate peak curve.

The scattering angle and the scattering intensity obtainable from the X-ray small angle scattering method resulted in non-uniform density
5 fluctuation to be observed.

The specific area was measured by the BET method, resulting in that the specific area was 50 m^2/g .

Other Analyses

10 The SIMS analysis resulted that the positive pole activating materials according to Preparation Methods 46 to 55 contained hydrogen and lithium. Also the dehydration peak of each TG (Thermogravimetric analysis), DTA (Differential Thermal Analysis) and
15 DSC (Differential Scan Thermal Heating Value Measurement) and the absorption spectrum of FTIR (Fourier Transform Infrared) resulted that a hydroxyl group was present. *in*

Comparative Preparation Method 46

20 A lithium-manganese oxide was prepared by the following method.

Powder of electrolyzed manganese dioxide manufactured by Mitsui Kinzoku and lithium carbonate were mixed with each other at a ratio of 1:0.4 and
25 they were heated at 800°C so that lithium manganese oxide was prepared.

The size of crystal grains was measured from

1 the half value width of the X-ray analysis curve and the
angle of diffraction in accordance with the Scherrer's
Equation. The size of the crystal grain was 600 Å or
larger.

5 The RHEED pattern resulted in a ring pattern in
which a spot pattern could be confirmed.

The X-ray radial distribution function resulted
in discontinuous peak curve.

The specific area was measured by the BET method,
10 resulting in that the specific area was 40 m²/g.

Comparative Preparation Method 47

A reagent manufactured by Wako was dried at 400°C
in a vacuum state.

The size of crystal grains was measured from the
15 half value width of the X-ray analysis curve and the
angle of diffraction in accordance with the Scherrer's
Equation. The size of the crystal grain was 800 Å.

The RHEED pattern resulted in a ring pattern in
which a spot pattern could be confirmed.

20 The X-ray radial distribution function resulted
in discontinuous peak curve.

The specific area was measured by the BET
method, resulting in that the specific area was
4 m²/g.

25 Comparative Preparation Method 48

A lithium-nickel oxide was prepared by the
following method.

1 A lithium carbonate and nickel nitrate were
mixed at an equal mol ratio of 1:1 and the mixture was
heated to 800°C so that a lithium-nickel oxide was
prepared.

5 The size of crystal grains was measured from
the half value width of the X-ray analysis curve and
the angle of diffraction in accordance with the
Scherrer's Equation. The size of the crystal grain was
2000 Å or larger.

10 The RHEED pattern resulted in a ring pattern
in which a spot pattern could be confirmed.

The X-ray radial distribution function resulted
in discontinuous peak curve.

15 The specific area was measured by the BET
method, resulting in that the specific area was 50 m²/g.
Comparative Preparation Method 49

A lithium-nickel-cobalt oxide was prepared by
the following method.

20 A lithium carbonate, nickel carbonate and
cobalt carbonate were mixed at a mol ratio of 10:3:7
and the mixture was heated to 900°C for 20 hours, as to
be decomposed so that a nickel-cobalt oxide was
prepared. AD

25 The size of crystal grains was measured from
the half value width of the X-ray analysis curve and
the angle of diffraction in accordance with the
Scherrer's Equation. The size of the crystal grain was

1 1100 Å or larger.

The RHEED pattern resulted in a ring pattern in which a spot pattern could be confirmed.

The X-ray radial distribution function
5 resulted in discontinuous peak curve.

The specific area was measured by the BET method, resulting in that the specific area was 40 m²/g.

Comparative Preparation Method 50

A vanadium-molybdenum oxide was prepared by
10 the following method.

A vanadium oxide and a molybdenum oxide were mixed at a ratio of 7:3, and the mixture was heated to 800°C in a platinum crucible, as to be melted and mixed. Then, the mixture was cooled gradually so that
15 the block-shape vanadium oxide and molybdenum oxide were prepared. They were crushed by a roller mill so that grains of vanadium oxide-molybdenum oxide were prepared.

The size of crystal grains was measured from
20 the half value width of the X-ray analysis curve and the angle of diffraction in accordance with the Scherrer's Equation. The size of the crystal grain was 700 Å or larger.

The RHEED pattern resulted in a ring pattern
25 in which a spot pattern could be confirmed.

The X-ray radial distribution function resulted in discontinuous peak curve.

$$i/M$$

5 A titanium sulfide was prepared by the
following method.

A titanium disulfide powder manufactured by Kojundo Kagaku was dried at 400°C in a vacuum state.

The size of crystal grains was measured from the half value width of the X-ray analysis curve and the angle of diffraction in accordance with the Scherrer's Equation. The size of the crystal grain was 900 Å or larger.

The RHEED pattern resulted in a ring pattern
15 in which a spot pattern could be confirmed.

The X-ray radial distribution function resulted in discontinuous peak curve.

The specific area was measured by the BET method, resulting in that the specific area was $50 \text{ m}^2/\text{g}$.

M=

A lithium-iron-cobalt oxide was prepared by the following method.

Lithium carbonate, iron acetate and cobalt carbonate were mixed at the same mole ratio, and decomposed at 600°C in air so that an iron cobalt oxide was prepared. Then, it was crushed by a ball mill so that grains were obtained.

1 The size of crystal grains was measured from
the half value width of the X-ray analysis curve and
the angle of diffraction in accordance with the
Scherrer's Equation. The size of the crystal grain
5 was 1000 Å or larger.

The RHEED pattern resulted in a ring pattern
in which a spot pattern could be confirmed.

The X-ray radial distribution function
resulted in discontinuous peak curve.

10 The specific area was measured by the BET
method, resulting in that the specific area was 40 m²/g.
Comparative Preparation Method 53

A manganese containing magnesium added thereto-
vanadium oxide was prepared by the following method.

15 A manganese dioxide, vanadium pentaoxide and
magnesium hydroxide were mixed at a mol ratio of 10:10:
1, and then they were decomposed at 700°C in air. As
a result, the manganese containing magnesium added
thereto-vanadium oxide was prepared. Then, they were
20 crushed by a ball mill so that grains were obtained.

The size of crystal grains was measured from
the half value width of the X-ray analysis curve and
the angle of diffraction in accordance with the
Scherrer's Equation. The size of the crystal grain
25 was 1300 Å or larger.

The RHEED pattern resulted in a ring pattern
in which a spot pattern could be confirmed.

1 The X-ray radial distribution function resulted
in discontinuous peak curve.

 The specific area was measured by the BET
method, resulting in that the specific area was 27
5 m^2/g .

Comparative Preparation Method 54

 A lithium-copper-cobalt oxide was prepared by
the following method.

 A lithium carbonate, cobalt carbonate and
10 copper carbonate were mixed at the same mol ratio, and
then they were decomposed at 600°C in air. As a
result, the manganese containing magnesium added
thereto-vanadium oxide was prepared. Then, they were
crushed by a ball mill so that grains were obtained.

15 The size of crystal grains was measured from
the half value width of the X-ray analysis curve and
the angle of diffraction in accordance with the
Scherrer's Equation. The size of the crystal grain
was 1100 \AA or larger.

20 The RHEED pattern resulted in a ring pattern
in which a pot pattern could be confirmed.

 The X-ray radial distribution function
resulted in discontinuous peak curve.

 The specific area was measured by the BET
25 method, resulting in that the specific area was 10
 m^2/g .

Analyzing Apparatus

1 The positive pole activating material prepared
by Preparation Methods 46 to 55 and Comparative
Preparation Methods 46 to 54 were analyzed by using
the following apparatuses. The X-ray diffraction
5 measurement was performed by using MXP3VA manufac-
tured by MacScience.

The RHEED measurement was performed by using
JEM-100SX manufactured by Nihon Denshi.

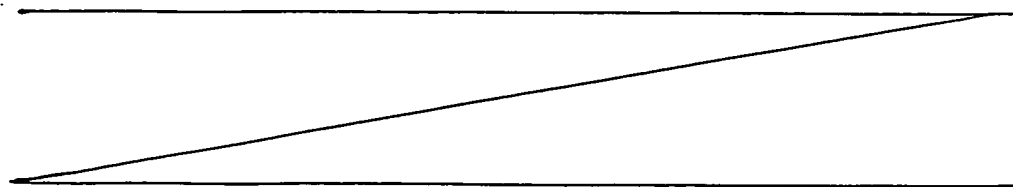
10 The specific area measurement by the BET
method was performed by using GEMIN12300 manufactured
by Micromeritex.

As a result of the comparisons between the
transition metal and the group ~~6A~~ element according to
Preparation Methods according to the present invention
15 and those according to Comparative Preparation Methods,
the compounds according to the present invention
exhibited smaller particle grain size as compared with
the results of Comparative Preparation Method, while
having an amorphous or microcrystal structure.

20 Manufacturing of Lithium Secondary Battery

Lithium secondary batteries were manufactured
by using the positive pole activating materials
prepared by the foregoing preparation methods.

25



VI
2

A

1 Example 46

5 which could be assembled simply and which had a cross
sectional shape schematically shown in Fig. 2.

10 the reverse side of the lithium metal foil. Then, the surface of lithium was covered with a fluoro-resin thin film by using thin solution of Lumiflon, which was a fluoro-resin paint manufactured by Asahi Glass, so that the negative pole was manufactured.

15 Acetylene black powder and xylene solution of
the Lumiflon, which was a fluoro-resin paint manufactured
by Asahi Glass, were mixed with the positive pole
activating material which was prepared by Preparation
Method 46 and which was lithium-manganese oxide. The
20 mixture was applied to the titanium mesh, and it was
hardened at 80°C, and then heated with microwaves.
As a result, the positive pole 203 was formed.

25 lithium salt in an equal quantity mixture solvent of
propylene carbonate (PC) and dimethoxyethane (DME).

The separator 208 was manufactured in such a

1 manner that a polypropylene separator having small
apertures was sandwiched by unwoven polypropylene
sheets.

The assembly was performed in such a manner that
5 the separator 208 was sandwiched between the negative
pole 201 and the positive pole 203, followed by
inserting them into a positive pole case 207 made of
titanium clad stainless steel. Then, the electrolytic
solution was injected. Then, the negative pole cap 206
10 made of the titanium clad stainless steel and the
insulating packing 210 made of fluorine rubber were used
for sealing so that the lithium secondary battery was
manufactured.

Example 47

15 The vanadium oxide prepared by Preparation
Method 47 was used as the positive pole activating
material, a battery having a cross-sectional shape
schematically shown in Fig. 2 was manufactured.

First, the nickel mesh collector was pressed
20 against the reverse side of the lithium metal foil in
an atmosphere of dry argon gas so that the negative
pole was manufactured.

Acetylene black powder and Super Konak F which
was a fluoro-resin paint manufactured by Nihon Yushi were
25 mixed with the vanadium oxide serving as the positive
pole activating material and prepared by Preparation
Method 2, followed by adding xylene by a small quantity.

1 The mixture was applied to the nickel mesh, and it was
hardened at 150°C. As a result, the positive pole was
manufactured.

Then, similar processes to those according to
5 Example 46 were performed so that the lithium secondary
battery shown in Fig. 2 was assembled.

Example 48

By using the positive pole activating material
prepared by Preparation Method 48, a battery which had
10 a simple structure, which could be assembled simply and
which had a cross-sectional shape schematically shown
in Fig. 2 was assembled.

First, the nickel mesh collector was pressed
against the reverse side of the lithium metal foil in
15 an atmosphere of dry argon gas so that the negative
pole was manufactured.

Acetylene black powder and tetrafluoroethylene
polymer powder were mixed with the lithium-nickel oxide
prepared by Preparation Method 48 and serving as the
20 positive pole activating material. The mixture was
pressed against the nickel mesh with heat, as to be 20
formed into the positive pole 203.

Then, similar processes to those according to
Example 46 were performed so that the lithium secondary
25 battery shown in Fig. 2 was assembled.

Example 49

The lithium-nickel-cobalt oxide prepared by

1 Preparation Method 49 was used as the positive pole
activating material so that the battery shown in Fig. 2
was manufactured by the process similar to that
according to Example 48.

5 Example 50

The vanadium-molybdenum oxide prepared by
Preparation Method 50 was used as the positive pole
activating material so that the battery shown in Fig.
2 was manufactured by the process similar to that
10 according to Example 48.

Example 51

The vanadium-molybdenum oxide prepared by
Preparation Method 51 was used as the positive pole
activating material so that the battery shown in Fig.
15 2 was manufactured by the process similar to that
according to Example 48.

Example 52

The titanium sulfide prepared by Preparation
Method 52 was used as the positive pole activating
20 material so that the battery shown in Fig. 2 was manu-
factured by the process similar to that according to
Example 48.

Example 53

The lithium-iron-cobalt oxide prepared by
25 Preparation Method 53 was used as the positive pole
activating material so that the battery shown in Fig. 2
was manufactured by the process similar to that

1 according to Example 48.

Example 54

The manganese containing magnesium added thereto-
vanadium oxide prepared by Preparation Method 54 was
5 used as the positive pole activating material so that
the battery shown in Fig. 2 was manufactured by the
process similar to that according to Example 48.

Example 55

The lithium-copper-cobalt oxide prepared by
10 Preparation Method 55 was used as the positive pole
activating material so that the battery shown in Fig. 2
was manufactured by the process similar to that
according to Example 48.

Comparative Example 46

15 By using the positive pole activating material
prepared by Comparative Preparation method 46, the
battery having a cross-sectional shape schematically
shown in Fig. 2 was manufactured.

First, the titanium mesh collector 200 was
20 pressed against the reverse side of the lithium metal
foil in an atmosphere of dry argon so that the negative
pole was manufactured.

Acetylene black powder and tetrafluoroethylene
polymer powder were mixed to the lithium-manganese oxide
25 prepared by Comparative Preparation Method 46 and
serving as the positive pole activating material, as to
be, with heat, pressed and formed into the positive pole

10

1 203.

Then, similar processes to those according to Example 46 were performed so that the lithium secondary battery was assembled.

5 Comparative Example 47

The vanadium oxide prepared by Comparative Preparation Method 47 was used as the positive pole activating material so that the battery shown in Fig. 2 was manufactured by the process similar to that
10 according to Example 48.

Comparative Example 48

The lithium-nickel oxide prepared by Comparative Preparation Method 48 was used as the positive pole activating material so that the battery shown in Fig. 2
15 was manufactured by the process similar to that according to Example 48.

Comparative Example 49

The lithium-nickel-cobalt oxide prepared by Comparative Preparation Method 49 was used as the
20 positive pole activating material so that the battery shown in Fig. 2 was manufactured by the process similar to that according to Example 48.

Comparative Example 50

The vanadium-molybdenum oxide prepared by
25 Comparative Preparation Method 50 was used as the positive pole activating material so that the battery shown in Fig. 2 was manufactured by the process similar

1 to that according to Example 48.

Comparative Example 51

The titanium sulfide prepared by Comparative
Preparation Method 51 was used as the positive pole
5 activating material so that the battery shown in Fig. 2
was manufactured by the process similar to that
according to Example 48.

Comparative Example 52

The lithium-iron-cobalt oxide prepared by
10 Comparative Preparation Method 52 was used as the
positive pole activating material so that the battery
shown in Fig. 2 was manufactured by the process similar
to that according to Example 48.

Comparative Example 53

15 The manganese containing magnesium added thereto-
vanadium oxide prepared by Comparative Preparation
Method 53 was used as the positive pole activating
material so that the battery shown in Fig. 2 was
manufactured by the process similar to that according
20 to Example 48.

Comparative Example 54

The lithium-copper-cobalt oxide prepared by
Comparative Preparation Method 54 was used as the
positive pole activating material so that the battery
25 shown in Fig. 2 was manufactured by the process similar
to that according to Example 48.

Evaluation of Performance of Lithium Secondary Battery

5 respect to the cycle life of the batteries according to
Comparative Examples.

10 pause for 30 minutes and a cut-off voltage of 1.0V was
applied. A charging/discharging apparatus HJ-101M6
manufactured by Hokuto Electric was used. The
charge/discharge test was commenced at discharge, the
battery capacity was ~~evaluate~~^{1.5} the quantity of the third
15 discharge, and the cycle life was evaluate^{1.5} by the number
of cycles when the battery capacity had deteriorated to
60% or less.

20 present invention and the comparative examples, that is,
the battery capacities and cycle life of the examples of
the present invention and the comparative examples were
evaluated as shown in Table 12 while making the
performance of the battery according to the comparative
25 example to be a reference value of 1.

As can be understood from Table 12, the comparisons made between Examples 46 to 55 and

1 Comparative Examples 46 to 54 resulted that the use of
the batteries according to the present invention enabled
the capacity of the battery to be enlarged and the cycle
life to be lengthened. *in*

5 Table 12

Examples	Comparative Examples	Capacity of Battery (Present Invention/ Comparative Example)	Cycle life (Present Invention/ Comparative Example)
10 Example 46	Comparative Example 46	2.3	4.8
Example 47	Comparative Example 47	3.1	3.2
Example 48	Comparative Example 48	2.1	1.7
15 Example 49	Comparative Example 49	2.0	1.4
Example 50	Comparative Example 50	4.1	2.9
Example 51	Comparative Example 50	3.2	2.1
Example 52	Comparative Example 51	2.4	1.4
20 Example 53	Comparative Example 52	2.3	1.5
Example 54	Comparative Example 53	1.7	2.0
Example 55	Comparative Example 54	2.2	1.8

25

Further, combinations of the embodiments of the
present invention will enable further improved secondary

1 battery to be obtained.

According to the present invention, if dendrite
of lithium or zinc grows at the time of charge, short
circuits between the negative pole and the positive pole
5 can be prevented. Therefore, a lithium secondary
battery, a nickel-zinc secondary battery and an air-zinc
secondary battery exhibiting a long charge/discharge
cycle life can be manufactured. Further, the metal
lithium can be used as the negative pole activating
10 material. Therefore, a secondary battery exhibiting a
high energy density can be manufactured while improving
safety.

Although the invention has been described in its
preferred form with a certain degree of particularity, it
15 is understood that the present disclosure of the
preferred form can be changed in the details of
construction and the combination and arrangement of
parts may be resorted to without departing from the
spirit and the scope of the invention as hereinafter
20 claimed.

1 ABSTRACT OF THE DISCLOSURE

2 A secondary battery exhibiting a long cycle life
3 and comprising a negative pole activating material made
4 of lithium or zinc is provided, the battery at least
5 having a negative pole made of lithium or zinc serving
6 as the negative pole activating material, an electrolyte
7 (electrolytic solution), a separator, a positive pole
8 made of a positive pole activating material, a
9 collecting electrode and a battery case, wherein at
10 least the surface of the negative pole is covered with
11 a film having a structure which allows ions relating to
12 the battery reactions to pass through. Since growth of
13 dendrite of lithium or zinc at the time of the charge
14 can be prevented, short circuit^{ing} between the negative
15 pole and the positive pole can be prevented. Therefore,
16 the charge/discharge cycle life can significantly be
17 lengthened. As a result, a lithium secondary
18 battery, a nickel-zinc secondary battery, an air-zinc
19 secondary battery, a bromine-zinc secondary battery and
20 a silver oxide-zinc secondary battery of the long cycle
21 life can be manufactured.